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<p>A background discussion of polymer viscoelasticity is given. Methods of polymer characterization are discussed. Factors in the compounding and vulcanization of elastomeric materials which affect end-product performance are also discussed.</p> <p>General information and cure systems are discussed for a number of different classes of rubber materials. Dynamic mechanical properties of a number of elastomeric materials are graphically presented. Compounding recipes and cure conditions are included, as well as the static physical properties. References to standard test methods (ASTM) are included where applicable. Indices containing names of suppliers of elastomeric materials and adhesives, as well as generic and trade-name cross-indexing, are also incorporated into this work.</p> <p>Additionally, an appendix on acoustical coupling fluids is included. This lists many of the</p>			
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Neoprenes,
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Polyurethanes. (AW)
Acoustic coupling fluids

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Fluids currently in use. Physical properties of interest, such as dielectric constant and electrical resistivity, as well as thermodynamic properties (where available) are included. Key words!



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CONTENTS

PREFACE.....	ix
ACKNOWLEDGMENTS.....	xi
LIST OF SYMBOLS.....	xiii
Chapter 1 - INTRODUCTION.....	01
1.1 SCOPE OF THE EFFORT.....	01
1.2 DYNAMIC PROPERTIES FOR ISOTROPIC, VISCOELASTIC MATERIALS.....	03
1.2.1 Elastic Moduli and Compliances.....	03
1.2.2 Relationships Between Moduli, Sound Speed, and Attenuation.....	08
1.3 INFLUENCE OF TEMPERATURE AND FREQUENCY.....	11
1.3.1 Time-Temperature Superposition.....	15
1.3.2 The Glass Transition.....	18
Chapter 2 - METHODS OF POLYMER CHARACTERIZATION.....	23
2.1 SYSTEMS FOR THE MEASUREMENT OF YOUNG'S AND SHEAR MODULI.....	24
2.1.1 Forced Vibration, Non-Resonant Techniques.....	25
2.1.2 Resonant Devices.....	29
2.2 BULK AND LONGITUDINAL BULK MODULI.....	32
2.2.1 Bulk Modulus.....	32
2.2.2 Longitudinal Bulk Modulus.....	33
2.2.3 Impedance Tubes.....	33
2.2.4 Ultrasonic Techniques.....	37
2.2.5 Pulse-Echo Methods.....	39
2.3 FOURIER TRANSFORM INFRARED (IR) SPECTROSCOPY.....	41
2.3.1 Basic Theory of Operation.....	41
2.3.2 Sampling Techniques.....	44
2.3.2.1 Transmission Spectroscopy.....	44
2.3.2.2 Reflection Techniques.....	46

2.3.2.3	<i>Photoacoustic Spectroscopy</i>	50
2.4	DIELECTRIC SPECTROSCOPY.....	51
2.5	THERMAL ANALYSIS.....	52
Chapter 3	- ELASTOMERIC MATERIALS.....	57
3.1	GENERAL INFORMATION.....	57
3.2	COMPOUNDING OF ELASTOMERS.....	57
3.2.1	Choice of Gum Stock.....	58
3.2.2	Cure Systems and Crosslinking.....	60
3.2.3	Effects of Crosslinking.....	61
3.2.4	Fillers.....	62
3.2.5	Plasticizers, Processing Aids, and Softeners.....	69
3.2.6	Antidegradents.....	70
3.3	VULCANIZATION AND MOLDING.....	74
3.4	ADHESION.....	80
3.5	BOND FAILURES.....	86
Chapter 4	- APPLICATIONS OF MATERIAL PARAMETERS TO DESIGN REQUIREMENTS.....	89
4.1	VIBRATION ISOLATION SYSTEMS.....	90
4.2	STRUCTURAL DAMPING.....	95
4.3	CONSTRAINED-LAYER DAMPING.....	97
Chapter 5	- BUTYL (IIR) AND CHLOROBUTYL (CIIR) RUBBERS.....	105
5.1	GENERAL INFORMATION.....	105
5.2	CURE SYSTEMS.....	107
5.3	FILLERS.....	116
Chapter 6	- ETHYLENE-PROPYLENE-DIENE MONOMER (EPDM).....	127
6.1	GENERAL INFORMATION.....	127
6.2	SPECIFIC FORMULATIONS.....	128

Chapter 7 - FLUOROCARBON RUBBERS (CFM).....	137
7.1 GENERAL INFORMATION.....	137
7.2 SPECIFIC FORMULATIONS.....	138
Chapter 8 - NATURAL RUBBER (NR).....	145
8.1 GENERAL INFORMATION.....	145
8.2 CURE SYSTEMS.....	146
8.3 SPECIFIC FORMULATIONS.....	149
Chapter 9 - POLYCHLOROPRENE (NEOPRENE) RUBBERS (CR).....	155
9.1 GENERAL INFORMATION.....	155
9.2 SPECIFIC FORMULATIONS.....	157
Chapter 10 - NITRILE RUBBERS (NBR).....	167
10.1 GENERAL INFORMATION.....	167
10.2 SPECIFIC FORMULATIONS.....	169
Chapter 11 - POLYURETHANES.....	189
11.1 GENERAL INFORMATION.....	189
11.2 COMMERCIALY AVAILABLE MATERIALS.....	192
<i>Polyurethane PR 1526</i>	202
<i>Polyurethane PR 1528</i>	203
<i>Polyurethane PR 1538</i>	204
<i>Polyurethane PR 1547</i>	205
<i>Polyurethane PR 1564</i>	206
<i>Polyurethane PR 1570</i>	207
<i>Polyurethane PR 1574</i>	208
<i>Polyurethane PR 1590</i>	209
<i>Polyurethane PR 1592</i>	210
<i>Polyurethane EN 5 (Conathane)</i>	211
<i>Polyurethane EN 9 (Conathane)</i>	212

<i>Polyurethane Hexcel Uralite 3140</i>	213
<i>Polyurethane Sorbothane</i> <i>(Shore 00, 50, and 70 Durometer)</i>	214
Chapter 12 - OTHER CLASSES OF RUBBER.....	215
12.1 POLYBUTADIENE (BR).....	215
12.2 CELOROSULFONATED POLYETHYLENE (HYPALON) (CSM).....	222
12.3 STYRENE-BUTADIENE RUBBER (SBR).....	223
Appendix 1 - GENERIC DESIGNATION CROSS INDEX.....	225
Appendix 2 - COMMERCIAL NAME CROSS INDEX.....	229
Appendix 3 - MANUFACTURERS OR SUPPLIERS INDEX.....	233
Appendix 4 - MANUFACTURERS OF ADHESIVES.....	237
Appendix 5 - TRANSDUCER FILL FLUIDS.....	243
A5.1 GENERAL INFORMATION.....	243
A5.2 CASTOR OIL.....	246
A5.3 ISOPAR.....	254
A5.3.1 Polyalkylene Glycol.....	255
A5.3.2 Polyalphaolefin.....	257
A5.3.3 Shell Sol 71.....	257
A5 3.4 Silicone Fluids.....	258
Appendix 6 - SOUND SPEEDS, DENSITIES, AND CHARACTERISTIC IMPEDANCES OF VARIOUS METALS.....	261
Appendix 7 - APPROXIMATE RELATIONSHIP BETWEEN SHORE A HARDNESS AND STATIC YOUNG'S MODULUS	263
Appendix 8 - SOME MECHANICAL AND PHYSICAL PROPERTIES OF VARIOUS ALLOYS.....	265
Appendix 9 - TYPICAL CORROSION RATES AND PITTING CHARACTERISTICS OF VARIOUS METALS AND ALLOYS IN SEAWATER.....	267
REFERENCES.....	269
GLOSSARY.....	291

FIGURE LOCATOR.....	295
TABLE LOCATOR.....	305
KEY WORD LOCATOR.....	309

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PREFACE

The original version of this compilation (published as NRL Memorandum Report 4311) was an attempt to collect and collate information on the static and dynamic properties of elastomeric materials in a format suitable for use by transducer design engineers. It was handicapped by a lack of complete information on many of the materials presented. The graphical format used was also somewhat awkward. The present edition hopefully represents an improvement upon this situation. It should prove useful to both scientists and design engineers. This book is not intended to be a complete treatment of polymer chemistry and/or physics. It is not written from a continuum mechanics approach, and is not mathematically sophisticated. Several treatments of polymer viscoelasticity, in particular the work of Ferry, are available for those who wish to pursue the subject in greater depth. Instead, the present work is designed to be used in a handbook format, and to serve as a source book for those who wish to pursue certain topics at a more involved level.

The intent of this work is to provide a guidebook rather than a cookbook. It is hoped that the results presented here will give the reader some insight into the interplay of various factors in the choice of a material for a given application. In particular, it may prove enlightening to some design engineers, who sometimes do not seem to recognize the constraints placed upon polymeric materials by basic physical laws. Apologies are tendered to those who may not find their favorite material(s) included in this compilation. It is not intended to function as a place where one simply looks up the right answer for a given type of problem. Rather, it is intended to serve as a convenient reference and a guide to further research in extending the capabilities of a given class of material.

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LIST OF SYMBOLS

a_T :	The ratio of relaxation times for an elastomer at some temperature T and a reference temperature T_R that is a characteristic temperature for the material under consideration, or the ratio of the shifted frequency to the reference frequency f_0 .
c_1^0, c_2^0 :	Coefficients for shift factor in the WLF equation referred to T_0 as reference temperature.
a :	Attenuation per unit length, nepers/m.
C :	Phase velocity for a given mode of wave propagation in a material, meters/s.
A :	Real component in complex propagation constant.
x_0 :	Critical damping distance.
e :	Base of real logarithms.
E^* :	Complex dynamic Young's modulus, Pa.
E' :	Young's storage modulus, Pa.
E'' :	Young's loss modulus, Pa.
D^* :	Complex extensional compliance, Pa^{-1} .
D' :	Real extensional compliance, Pa^{-1} .
D'' :	Loss compliance in extension, Pa^{-1} .
G^* :	Complex dynamic shear modulus, Pa.
G' :	Shear storage modulus, Pa.
G'' :	Shear loss modulus, Pa.
J^* :	Complex shear compliance, Pa^{-1} .
J' :	Real shear compliance, Pa^{-1} .
J'' :	Shear loss compliance, Pa^{-1} .
K^* :	Complex bulk modulus, Pa.
K' :	Bulk storage modulus, Pa.
K'' :	Bulk loss modulus, Pa.
B^* :	Complex bulk compliance, Pa^{-1} .

(continued)

LIST OF SYMBOLS (continues)

B' :	Real part of bulk compliance, Pa^{-1} .
B'' :	Storage bulk compliance, Pa^{-1} .
M^* :	Complex longitudinal modulus, Pa.
M' :	Longitudinal storage modulus, Pa.
M'' :	Longitudinal loss modulus, Pa.
δ :	Phase angle between stress and strain.
$\tan \delta$:	Mechanical loss factor, expressed as ratio of loss modulus to storage modulus or loss compliance to storage compliance.
ω :	circular frequency, rad/s.
f :	Frequency, Hz.
λ :	Wavelength, m.
σ :	Used as symbol for shear stress in sinusoidal deformation in Ch. 1.2.1.
ϵ :	Tensile strain.
ρ :	Density, kg/m^3 .
T :	Temperature, $^{\circ}\text{C}$ or K. Also, value of transmissibility, dB (Ch. 4).
T_g :	Glass transition temperature.
P :	Pressure, Pa.
α_P :	Ratio of relaxation times at a pressure P to a reference pressure, P_0 .
V :	Volume, m^3 .
B :	Empirical constant in equation for pressure dependence of relaxation times of polymers.
η :	Structural loss factor for composite damping structure.
η^* :	Complex shear viscosity, G''/ω .
θ :	Angle of incidence.
μ :	Poisson's ratio.

(continued)

LIST OF SYMBOLS (continues)

- γ : Used as symbol for shear strain in sinusoidal deformation in Ch. 1.2.1.
- ϵ^* : Complex dielectric constant.
- ϵ' : Real component of complex dielectric constant.
- ϵ'' : Imaginary component of dielectric loss.

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CHAPTER 1

INTRODUCTION

1.1 SCOPE OF THE EFFORT

Polymeric materials have been used in a variety of applications for the absorption, transmission, or detection of sound. Examples of this are vibration isolators and vibration dampers, loudspeaker cones and surrounds, and sonar transducer passive elements. More exotic applications have utilized^{1,2} the effects of polymeric coatings upon acoustically induced phase shifts in optical fibers used as interferometers for underwater acoustical detection systems.

All of these situations have in common their reliance upon the viscoelastic nature of polymeric materials. This work will concern itself primarily with a specialized group of high polymers, known as elastomeric materials. The phrases *elastomeric* and *rubber-like* will be used interchangeably in the present case. While all rubbers are elastomers, not all elastomers are rubbers. The distinction as explained in the American Society for Testing and Materials (ASTM) Standard D 1566 is based on both the length of time required for a deformed sample to return to its approximate original shape after removal of the deforming force and the extent of that recovery. Elastomers as a group are characterized by large deformability, low shape rigidity, large energy-storage capacity, high mechanical hysteresis, pressure-temperature dependence of density, and as a critical behavioral aspect, by variations in dynamic stiffness as a function of specimen geometry, temperature, pressure, and frequency. References 3 through 5 provide a more detailed treatment of the novel engineering properties of elastomers, as contrasted to more linear types of materials such as metals. The properties of an elastomer will depend upon the base polymer chosen, curing time and temperature, processing conditions, additives, molecular weight and its distribution, compounding technique, and sample fabrication. All of these factors make the optimization of an elastomeric material for a specific application a difficult task. The degree of difficulty is often made larger by the fact

that the choice of an elastomer may be determined primarily by its non-acoustical engineering properties (i.e., bondability, environmental resistance, and tensile properties).

This situation is frequently encountered in situations dealing with underwater acoustics. An additional complicating factor is often introduced by the fact that proprietary materials may be used in acoustical systems, with subsequent (and often undisclosed) changes in formulations, compounding or fabrication techniques causing undesired changes in the performance of the transduction or vibration control device.

In an effort to ameliorate some of these difficulties, a collection of information and data relating to various types of polymers used in acoustical applications is presented here. Although the thrust of the effort is slanted more towards underwater acoustical application, it is hoped that the compilation will also be helpful to those individuals concerned with the application of polymeric materials in other types of systems. In the present work, data are taken from unclassified, published literature and from unclassified results of research efforts supported by the Sonar Transduction Sciences Program and the Sonar Transducer Reliability Improvement Program (STRIP) in this and other Navy laboratories.

The intent here is to provide a guidebook rather than a recipe book. The rationale for this is that exact duplication of results presented for formulations in this compilation will require very careful attention to the conditions for mixing and curing to avoid variations from batch to batch. Instead, it is hoped that the material presented here will enable the reader to gain insight into the role of the interplay of various factors involved in the choice of a material for a particular application. To this end, a discussion of a number of topics dealing with polymeric materials is incorporated. None of these are treated in an encyclopedic or exhaustive fashion. The treatments shall serve as a brief review for those already familiar with the field, and provide sufficient information and additional references to other literature to allow novices in a given area to further familiarize themselves with it. These topics include a discussion of the

various dynamic moduli, methods of polymer characterization, elastomer compounding and molding, and adhesion; as well as a compilation of data both from research efforts in this laboratory and published literature. Formulations and cure conditions for the non-proprietary elastomers listed are included, as well as appendices for the listings of various names of elastomers and cross-referencing the generic, trade, and manufacturers' names (Appendices 1 through 3). Appendix 4 contains a directory of manufacturers of adhesives. Information on transducer fill fluids can be found in Appendix 5. Appendix 6 contains a compilation of sound speed data on various metals. The relationship between Shore A hardness and static Young's modulus for elastomers is depicted graphically in Appendix 7. Appendix 8 gives corrosion characteristics for various methods and alloys that may be used in underwater applications.

1.2 DYNAMIC PROPERTIES FOR ISOTROPIC, VISCOELASTIC MATERIALS

1.2.1 Elastic Moduli and Compliances

Many solids, such as metals and ceramics, exhibit primarily elastic effects when deformed to low levels of strain. Their behavior closely approximates that of a linear elastic material in that the induced components of strain are independent of strain history and rate of application of loading, and are proportional to the stresses that produce the deformation. Under low-amplitude, sinusoidal stress these materials behave essentially as Hookean solids, so that the resulting strain is in phase with the stress, the imparted energy is recoverable and not dissipated as heat, and the ratio of stress amplitude to strain amplitude is independent of frequency and equal to the appropriate elastic modulus for a given mode of deformation. The dynamic mechanical properties of these materials are specified by the appropriate elastic moduli or compliances⁶⁻⁸. In contrast, many liquids show appreciable viscous effects. Under normal conditions, they will behave as Newtonian fluids, where the rate of deformation is linearly related to rate of stress. The stress and strain are always $\pi/2$ radians out of phase, and much of the energy transferred to the liquid is dissipated as heat. If the rate of

deformation is not linearly related to the stress, the fluid is said to be non-Newtonian. Many polymeric solutions and molten polymers fall into this category.

High polymers are an intermediate class of material in which both appreciable elastic and viscous effects may be present under ordinary conditions of sinusoidally varying stress. At small strains under essentially isothermal conditions, polymers approximate a linear viscoelastic medium⁹ in mechanical behavior. The structural features responsible for this behavior can be modeled by various combinations of linear elastic elements (springs) and viscous elements (dashpots)⁹⁻¹². Both longitudinal and transverse acoustic waves can be propagated in a viscoelastic medium. As will be subsequently discussed, the expressions for the moduli governing the propagation of acoustic waves in a viscoelastic medium under the appropriate boundary conditions closely resemble those of an ideal, isotropic solid, with the elastic moduli being replaced with the corresponding frequency-dependent complex moduli.

The dynamic mechanical properties of many polymeric materials are independent of the direction of measurement. This classification of isotropic materials includes polymeric rubbers and glasses whose amorphous structures have molecular chain segments randomly oriented within the material. All of the materials included in this work fall within this classification; thus discussion is limited to isotropic materials. Within this context, a material will be said to be isotropic if the properties at a given point do not vary with the direction or orientation of the coordinate axes, while homogeneity requires that the properties not vary with position. Two material constants (i.e., G^* and K^*) are sufficient to characterize such materials. In the discussion that follows, it will be assumed that we are dealing with small strains and linear viscoelastic behavior. The reader is referred elsewhere¹³⁻¹⁵ for a discussion of measurements of the properties of anisotropic materials.

One of the simplest types of viscoelastic behavior, the uniform deformation of an elastomer under a sinusoidal shear stress, is illustrated in Fig. 1.1a. In this case, the strain, γ , lags behind the stress, σ ,

[Fig. 1.1b] with a phase angle, δ , which is between 0 and $\pi/2$ radians. The stress may be resolved into two components, one in phase and one $\pi/2$ radians out of phase with the strain. This enables us to decompose^{9,12} the complex shear modulus, G^* , into two vector components. These are the storage or elastic shear modulus, G' , and the viscous or loss shear modulus, G'' .

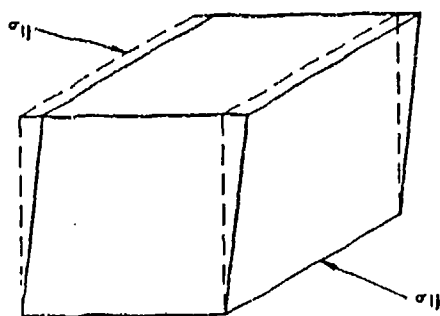


Fig. 1.1a - Simple shear deformation of an isotropic, viscoelastic element

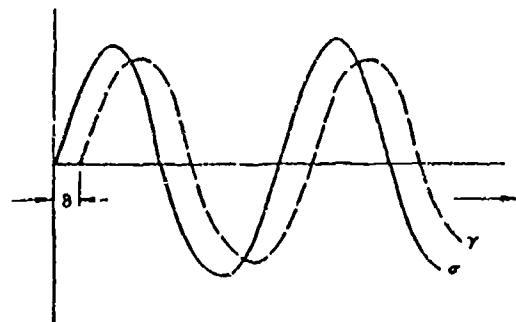
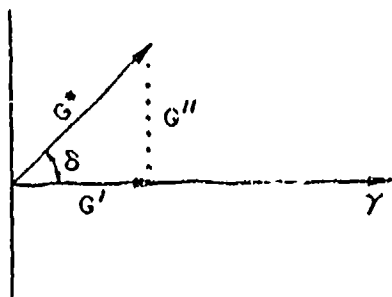


Fig. 1.1b - Time profile of sinusoidal stress and strain

It is evident from Fig. 1.1c that G' is the ratio of the stress in phase with the strain to the strain, while G'' is the ratio of stress out of phase with the strain to the strain. The ratio of G'' to G' is the tangent of the phase angle, δ , and is commonly denoted as the loss factor or loss tangent. It is also a measure of the internal damping of the polymer.



$$G^*(T, f) = G' + iG''$$

$$\tan \delta = \frac{G''}{G'}$$

Fig. 1.1c - Vectorial resolution of complex shear modulus in sinusoidal deformation

Alternatively, the data from sinusoidal shear experiments may be expressed in terms of a complex shear compliance, $J^* = J' - j J''$. Although the complex compliance, J^* , is reciprocally related to the complex shear modulus, G^* , the same is not true for their individual components. They are related by the following equations⁹:

$$J' = G' / (G'^2 + G''^2) = (1/G') / (1 + \tan^2 \delta) \quad (1)$$

$$J'' = G'' / (G'^2 + G''^2) = (1/G'') / [1 + (\tan^2 \delta)^{-1}] \quad (2)$$

with exactly analogous expressions being obtained for G' and G'' in terms of J' and J'' .

A second type of fundamental deformation [Fig. 1.2a] that an elastomer may experience is one in which the dimensions of an isotropic sample are increased or decreased uniformly by the application of normal forces over all its surfaces (i.e., hydrostatic pressure). The complex modulus describing this volume deformation in which no shape change takes place is the bulk modulus, K^* . The complex bulk modulus, K^* , and bulk compliance, B^* , may be defined in an exactly analogous way as for shear, with $K^* = K' + jK''$, and $B^* = B' - jB''$. In the most general case,

$$B_x = -V(\partial P / \partial V)_x, \quad (3)$$

where x is indicative of the conditions of the experiment. If x represents constant entropy, S , then the modulus corresponds to the adiabatic bulk modulus arising when bulk modulus is measured under dynamic conditions. If x represents constant temperature, T , then the modulus corresponds to the isothermal bulk modulus measured under static conditions⁷. In dynamic bulk modulus measurements the deformations are ordinarily very small and fall within the range of linear behavior. The change in free volume of an elastomer during a deformation cycle is a very small fraction of the total free volume. The modulus measured in bulk deformations has a relatively narrow range of magnitudes when measured over a wide range of temperatures

and frequencies. From a molecular standpoint, the viscoelastic behavior depends only on local motions of the polymer molecules, with entanglements and crosslinks making no contributions⁹.

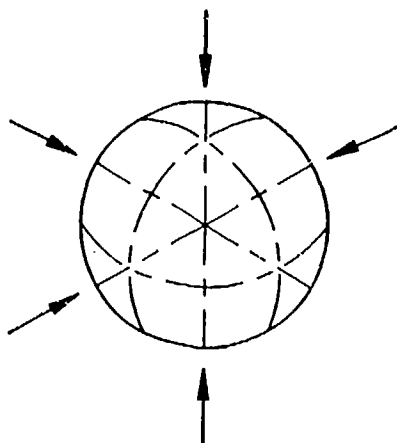


Fig. 1.2a - Bulk compression

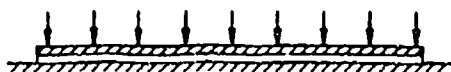


Fig. 1.2b - Bulk longitudinal deformation



Fig. 1.2c - Simple extension

A third type of deformation occurs [Fig. 1.2b] when the dimensions of a sample change in one direction and are constrained to be constant in the other two mutually perpendicular directions. The modulus corresponding to this mode of deformation is the bulk longitudinal modulus, M^* , and has components of both a bulk and a shear modulus ($K^* + 4/3 G^*$). In practice, it is normally observed^{9,16,17} that the longitudinal modulus will be dominated by bulk or volume deformational effects, so that it is a close approximation to the bulk modulus at relatively low (<100 kHz) frequencies. At higher frequencies or lower temperatures, the shear modulus component will be a substantial component of the dilatational modulus.

A fourth modulus arises for the case where ordinary longitudinal acoustic waves with a sinusoidal frequency dependence are propagated along a sample whose lateral dimensions are small compared to a wavelength [Fig. 1.2c]. This deformation in simple extension is characterized by the complex Young's modulus. The elastic restoring force associated with this deformation is the tensile relaxation or Young's storage modulus, which is given by $9 G'K'/(G' + 3K')$. Analogous to the shear case, a complex modulus ($E^* = E' + jE''$) and compliance ($D^* = D' - jD''$) may be defined.

Measurements in extension are easy to perform experimentally but have the disadvantage of simultaneous changes in both shape and volume. This makes the observed behavior more difficult to interpret on a molecular basis. However, for many polymers it is found that $K' \gg G'$ over a wide range of frequencies. In this case, $E' = 3G'$ and $D' = J'/3$, so that an experiment performed in simple extension gives the same information as one performed in simple shear.

The relationship between E' and G' can be expressed in terms of a dimensionless variable, $\mu = 1/2 [1 - (1/V)(\partial V/\partial \epsilon)]$, known as Poisson's ratio. The quantity ϵ in the preceding expression is the tensile strain for elongation. For rubbery materials, it is normally found^{9,14,17} that $K' \gg G'$, so that the real part of μ is very nearly $1/2$. The Poisson's ratio itself is, in theory, a complex quantity, although there have been relatively few experimental determinations of this^{18,19}. The relationships between G^* , K^* , M^* , E^* , and μ^* are discussed in Refs. 7, 9, and 14.

1.2.2 Relationships Between Moduli, Sound Speed, and Attenuation

Acoustic techniques have been widely used for determining the various dynamic moduli previously discussed. The effective dynamic moduli for rubber-like materials are normally much larger than the static moduli derived from stress-strain curves, and are found to be particularly dependent upon temperature and frequency. The commonly used experimental procedure for obtaining information concerning mechanical relaxation effects in polymers consists of measuring the appropriate parameters,

namely the sound velocity and attenuation, for elastic wave propagation in a sample of the appropriate geometry. A more complete discussion of measurement methods will be given in a later section.

In the case of linear vibrations, the equation describing the behavior of a sample with appropriate boundary conditions is²⁰

$$\nabla^2 \phi = \frac{1}{c^2} \left[\frac{\partial^2 \phi}{\partial t^2} + k \frac{\partial \phi}{\partial t} \right], \quad (4)$$

where ϕ is the deviation of a local value from the average in the neighborhood and represents the disturbance being propagated, c represents the velocity of propagation of the disturbance, and k is a dissipation term. The example considered in the present case is a plane shear wave, although the discussion would apply equally well to a longitudinal wave.

An appropriate solution to Eq. (4) for the case of a wave with angular frequency ω , amplitude A , sinusoidal time dependence, and exponential damping is

$$A_x = A_0 e^{i\omega t} e^{-(\alpha + i\omega/c)x}, \quad (5)$$

where α is the reciprocal of the distance, x_0 , within which the amplitude falls by a fraction of $1/e$, and the quantity ω/c is equal to a wavelength of sound in the material. It can be shown^{9,17,21} that components of the complex modulus may be calculated from determinations of either phase velocity, c , and attenuation, α , or wavelength, λ , and attenuation, through the relations

$$G' = \rho c^2 (1 - r^2) / [(1 + r^2)]^2, \quad (6)$$

and

$$G'' = 2\rho c^2 r / [(1 + r^2)]^2, \quad (7)$$

when $r = a\lambda/2\pi$. Also,

$$\tan \delta = 2r/(1 - r^2). \quad (8)$$

In some instances, it may be desired to calculate the propagation velocity and attenuation for a given type of wave from a knowledge of either the storage modulus and loss modulus or the storage modulus and loss tangent. Since the modulus is a complex quantity of the form

$$R^* = R' + jR'' = C^{*2} \rho, \quad (9)$$

where R denotes a generic modulus and

$$C^* = C \left(\frac{1 + jaC/\omega}{1 + \alpha^2 C^2/\omega^2} \right), \quad (10)$$

we may use Eqs. (9) and (10) to solve for the magnitude of the phase velocity and attenuation. Doing so yields

$$C^2 = \frac{2 [(R')^2 + (R'')^2]}{\rho \left[[(R')^2 + (R'')^2]^{1/2} + R' \right]}, \quad (11a)$$

$$C^2 = \frac{2 R'}{\rho \left[\sqrt{(1 + \tan^2 \delta)} + 1 \right]}, \quad (11b)$$

$$\alpha^2 = \frac{\omega^2 \rho \left[\sqrt{(R')^2 + (R'')^2} - R' \right]}{2 [(R')^2 + (R'')^2]}, \quad (12a)$$

$$\alpha^2 = \frac{\rho \omega^2}{2R'} \frac{\sqrt{(1 + \tan^2 \delta)} - 1}{1 + \tan^2 \delta}, \quad (12b)$$

where ω is the angular frequency and ρ is the density of the material.

Therefore, by inserting the real and imaginary components of the appropriate modulus, or real modulus and loss tangent, into Eqs. (11) and (12), the magnitude of the sound velocity and attenuation in the material may be calculated. In the case of low-loss materials where $\tan \delta \ll 1$, the expressions for velocity and attenuation simplify to

$$c \approx \sqrt{\frac{R'}{\rho}}, \quad (13a)$$

and

$$\alpha \approx 0.5 \omega \sqrt{\frac{\rho}{R'}} \cdot (\tan \delta). \quad (13b)$$

For materials with very high losses ($\tan \delta \gg 1$), the limiting approximations become

$$c \approx \sqrt{\frac{R'}{\rho} \cdot (2 \tan \delta)}, \quad (14a)$$

$$\alpha \approx 0.5 \omega \sqrt{\frac{\rho}{R'} \cdot \frac{2}{\tan \delta}}. \quad (14b)$$

1.3 INFLUENCE OF TEMPERATURE AND FREQUENCY

Since the dynamic response of a viscoelastic material will vary as both a function of temperature and frequency, it may be measured for a particular specimen geometry either as a function of frequency (or time) at a constant temperature or as a function of temperature at a fixed frequency of excitation. Only a small range of viscoelastic behavior will manifest itself during an experimentally accessible frequency range. Since it is not feasible to directly measure the complete viscoelastic response of a

material as a function of frequency at a constant temperature, it is clearly desirable to be able to construct such a curve from experimentally determined responses over a narrow range of frequencies at different temperatures.

Four different regions of dynamic mechanical behavior as a function of temperature and frequency can generally be distinguished for a viscoelastic material¹⁴. These are: (1) a low-temperature, glassy region where the storage modulus is a large, almost constant value; (2) a glass-rubber transition region where the storage modulus changes rapidly with temperature and/or frequency; (3) a rubbery region where the modulus varies slowly with temperature or frequency; and (4) a flow region where the modulus drops very rapidly (not all materials will exhibit flow behavior, since this is very much influenced by the crosslinking and molecular weight).

The loss tangent follows a different pattern; it is almost constant in the glassy region where the amorphous chain conformations of a polymer are generally frozen into a rigid network, so that a high storage modulus and low loss tangent are found. However, it is possible that one or more secondary transitions of low magnitude may arise from limited movement either within the main chain or within side groups attached to the chain¹⁴. The onset of the glass-rubber transition is characterized by a pronounced loss tangent peak. In the rubbery region, the loss tangent again decreases to a plateau value, increasing slightly with increasing frequency or decreasing temperature. The general behavior discussed here is summarized schematically in Fig. 1.3.

The behavior of the curves representing the modulus and loss tangent of a viscoelastic material, plotted logarithmically as a function of frequency or linearly as a function of temperature, as in Fig. 1.3, is analogous to the behavior observed in similar plots of the real and imaginary components of the dielectric constant for a dielectric material. The simultaneous occurrence of a rise in the real part of the modulus and a peak in the loss tangent as a function of temperature and frequency is a general property of viscoelastic materials known as the Kramers-Kronig dispersion

relationships. Under conditions of linearity and causality, they are normally expressed as integral relationships²² between the real and imaginary parts of the modulus that are a type of Hilbert transform.

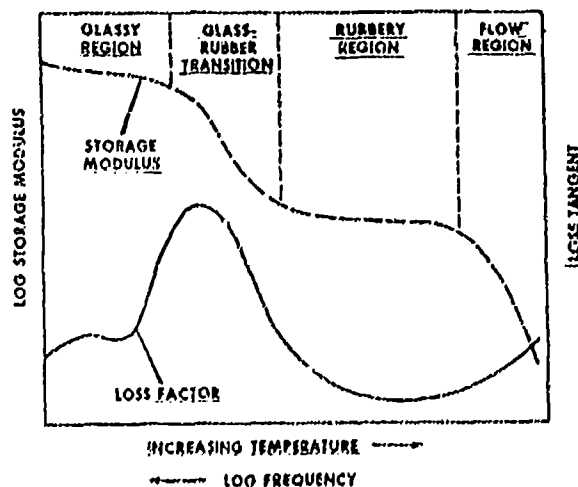


Fig. 1.3 - Variation of storage modulus and loss tangent with temperature and frequency for a viscoelastic material

Figures 1.4 and 1.5 illustrate the variation observed with temperature and frequency for the storage Young's modulus and loss tangent of a chlorobutyl rubber. Using the curves at 283.15 K as a reference, we note that an increase in temperature to 293.15 K causes the curves in both E' and $\tan \delta$ to shift to higher frequencies, with only minor changes in levels. This shift is a multiplicative factor in frequency, so that the dynamic mechanical property curve shifts are simply translations along the logarithmic frequency axis, with only slight vertical shift factors due to the effects of density and temperature changes upon intermolecular forces⁹. In a similar fashion, lowering the temperature to 273.15 K translates the property curves to lower frequencies. Materials that exhibit this type of behavior are said to be "thermo-rheologically simple". For a typical elastomeric material used in the frequency region corresponding to the rubber-to-glass transition, a shift to a higher temperature brings about a lower modulus, while a shift to a lower temperature gives a higher modulus. Nolle²³ has treated the behavior of viscoelastic materials as two-dimensional surfaces, showing the modulus and loss tangent as simultaneous functions of temperature and frequency. These illustrate that the storage

modulus increases with increasing frequency or decreasing temperature, while the loss tangent exhibits a maximum when considered as a function of temperature or of frequency.

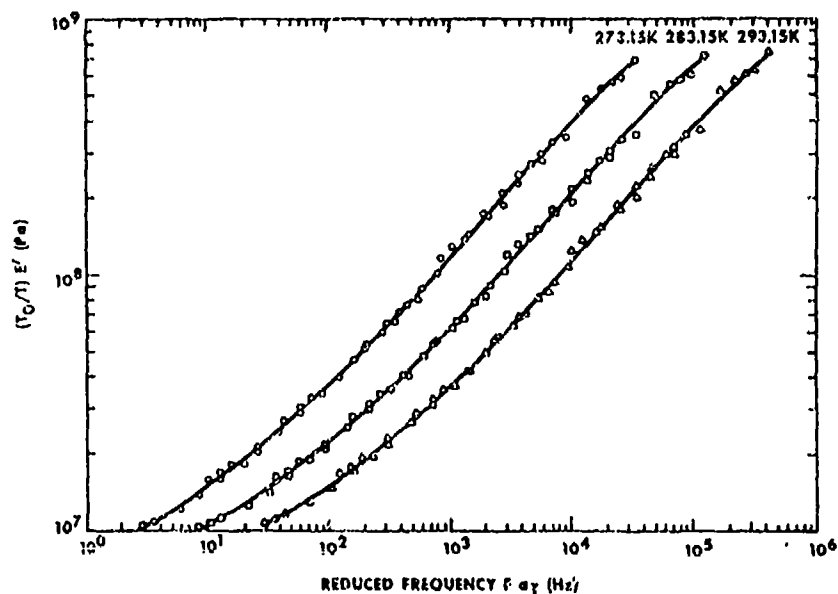


Fig. 1.4 - Plot of storage Young's modulus vs reduced frequency at three different temperatures for a resin-cured chlorobutyl reinforced with 85 phr of N847 black

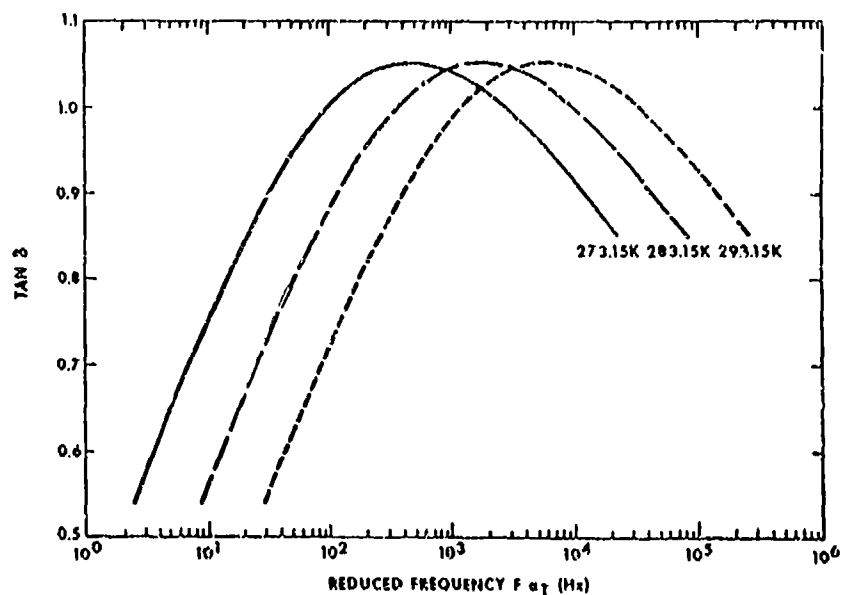


Fig. 1.5 - Plot of loss tangent vs reduced frequency at three different temperatures for a resin-cured chlorobutyl reinforced with 85 phr of N847 black

1.3.1 Time-Temperature Superposition

The interrelation between the dependence of the storage modulus and loss tangent, or storage modulus and loss modulus, upon both temperature and frequency (or time) can be expressed in terms of the time-temperature or frequency-temperature superposition principle^{9,24}. This principle, simply stated, says that there is an interrelated dependence upon frequency and temperature of the behavior of viscoelastic materials subjected to a periodically varying stress, or between time and temperature when subjected to a static stress over an extended period of time. In the present instance, we are considering frequency-dependent excitation. If we view the situation in a phenomenological manner, so that the temperature of a viscoelastic material is increased while it is maintained at a constant frequency of excitation, its internal molecular arrangement changes to a more mobile configuration and the material becomes more compliant. Conversely, a reduction in temperature causes a reduction in molecular mobility, so that the material stiffens and exhibits glass-like properties.

If the elastomer is maintained at a constant temperature and the stress frequency is changed, a related but inverse phenomenon occurs. For low frequencies, the period of stress is long enough so that the molecules have enough time to coil and uncoil. The behavior of the material is therefore rubber-like. At high frequencies, the period of stress is very small so the material does not have time to completely relax. It remains stiff and resembles a glass in its mechanical properties. Therefore, the correspondence between frequency and temperature for viscoelastic behavior is that a decrease in temperature at constant frequency causes the same change in dynamic properties of an elastomer as an increase in frequency at a constant temperature.

The composite parameter normally used to express the temperature-frequency dependence is the shift factor, a_T , where a_T is a monotonically decreasing function of temperature^{9,24}. The modulus, E' , and loss tangent, that one would observe at a reference temperature, T_0 , relative to an experimentally measured modulus and loss tangent at some temperature, T , are given by

$$E'(f, T_0) = (T_0 \cdot \rho_0 / T \cdot \rho) \cdot E'(fa_T, T) \quad (15a)$$

and

$$\tan \delta(f, T_0) = \tan \delta(fa_T, T). \quad (15b)$$

The correction ratio involving temperatures in the above expression is included because the modulus is directly proportional to T . Similarly, a correction for densities is included because the volume of a polymer is a function of temperature, and the modulus, which is defined per unit of cross-sectional area, will vary with the amount of material contained in a unit volume. Under normal circumstances, the correction for the changes in densities is a minor one⁹.

In the case of a material at two different temperatures T_1 and T_2 , where T_1 is less than T_2 , the dynamic mechanical properties are expressed as

$$E'(fa_{T_1}, T_1) = (T_1 \cdot \rho_1 / T_0 \cdot \rho_0) \cdot E'(f, T_0), \quad (16a)$$

$$\tan \delta(fa_{T_1}, T_1) = \tan \delta(f, T_0), \quad (16b)$$

$$E'(fa_{T_2}, T_2) = (T_2 \cdot \rho_2 / T_0 \cdot \rho_0) \cdot E'(f, T_0), \quad (16c)$$

and

$$\tan \delta(fa_{T_2}, T_2) = \tan \delta(f, T_0). \quad (16d)$$

For a given frequency f , $f a_T$ will be smaller at the higher temperature. Since the ratio $T_1 \rho_1 / T_2 \rho_2$ is approximately equal to one, the properties found at f and T_1 will be shifted at T_2 to a frequency that is dependent upon the ratio a_{T_1} / a_{T_2} . Since the storage modulus is a monotonically increasing function of frequency, a material will be softer at a higher temperature for a given frequency. Likewise, the peak in the loss tangent curve will shift to higher frequencies as the temperature is increased.

The amount of frequency shift required to superimpose a curve measured at some temperature, T , onto another curve at a reference temperature, T_0 , is analytically expressed for many polymers by the Williams-Landel-Ferry (WLF) equation^{9,24}:

$$\log a_T = \frac{-C_1 \cdot (T - T_0)}{C_2 + (T - T_0)} . \quad (17)$$

Here, the previously defined shift factor, a_T , may be viewed as either being equal to the ratio of the shifted frequency to the reference frequency, f_0 , or the ratio of relaxation times for a polymer at some temperature, T , and a temperature, T_0 , that is a characteristic temperature for the material under consideration. The constants c_1 and c_2 are characteristic for each polymer at a given T_0 . It has been found^{9,25,26} that some materials do not obey the WLF equation as written in Eq. (17), so that it is necessary to modify it with an energy term of the form

$$\log a_T = \frac{\Delta H}{R} \cdot \left[\frac{1}{T} - \frac{1}{T_0} \right] , \quad (18)$$

where the parameter ΔH represents an apparent activation energy for viscoelastic relaxation. Another more empirical function used for a large number of materials is of the form²⁷

$$a_T = [1 + (T - T_0)/278]^{-14} , \quad (19)$$

where T_0 is expressed in degrees Fahrenheit. The use of operators and fractional derivatives in the treatment of temperature shift functions and viscoelastic properties of elastomers has been treated by Rogers^{23,29}.

For a more complete exposition of time-temperature superposition and its theoretical justification in terms of free-volume theories of polymers, it is recommended that the reader consult Ref. 9. This reference also discusses the construction of extended master frequency curves from experimental data. At this point, it is worth noting that some care should be used in interpreting such a reduced curve in terms of actual physical behavior at the frequency extremes. It is possible to shift experimentally determined points over many decades of frequency. At the high-frequency end, this might range past 10^8 Hz. Since any error in the shifted points would tend to be cumulative, alternative techniques (such as Brillouin spectroscopy²⁶) should be used if possible to investigate molecular behavior in this range. Very low frequencies ($<10^{-8}$ s⁻¹) on a reduced scale would correspond to a time scale of years, with concomitant chemical changes occurring in the polymer that would invalidate any extrapolations from a master frequency curve. As long as reasonable care is used, the reduced curves can be used to predict properties over a wide range of temperatures and frequencies.

In the present work, modulus-frequency master curves are plotted on a logarithmic scale. The curves are normally presented at a reference temperature of 10°C. Values of the modulus and/or loss tangent at a given frequency can then be read directly from the graph, since the values of a_T and the temperature ratio will both be unity. Polynomial coefficients for fits of modulus-frequency and loss tangent-frequency curves in logarithmic form are also given for some of the materials presented.

1.3.2 The Glass Transition

The glass transition temperature, T_g , of an amorphous substance may be defined as the point at which the slope of the coefficient of thermal expansion as a function of temperature undergoes a discontinuity. The

glass transition itself is not a true first-order transition in the thermodynamic sense.

The phrase "glass transition" is sometimes used in an ambiguous sense as it relates to the study of polymer viscoelasticity. The value of T_g as determined by calorimetric methods is not a function of frequency and often differs in value from that determined by very low-frequency dynamic measurement techniques. A more appropriate term⁹ for transition temperatures determined in this manner might be the midpoint temperature, defined as either the point where $\tan \delta$ reaches a maximum as a function of temperature at a fixed frequency or the point at which the storage modulus reaches an arbitrarily assigned value (G' or $E' = 10^8$ Pa). Transition temperatures determined for polymeric materials at low frequencies (1 Hz) in this fashion are normally some 15°C higher than those determined by calorimetric methods (e.g., differential scanning calorimetry).

As previously discussed in regard to Fig. 1.3, the slope of the viscoelastic functions in the glass-rubber transition region are roughly similar for all polymer systems. However, the feature that varies greatly among different classes of polymers is the position on the frequency scale when different polymers are examined either at the same temperature or at suitable corresponding temperatures⁹. Similarly, variations in the temperature behavior of different polymers are found if they are examined at a fixed frequency. For example, the glass-to-rubber transition zone occurs at relatively low temperatures for flexible polymer chains such as silicones, but the converse is true for polar materials such as poly vinyl chloride.

The glass-rubber transition is normally insensitive to molecular weight unless the polymer is of very low molecular weight⁹. It is also relatively unaffected by crosslinking at low levels of crosslinking. The location of the glass-to-rubber transition zone, either as a function of frequency on a fixed temperature scale or as a function of temperature at a fixed frequency, is very important information from the standpoint of acoustic design. Optimization of a material for a specific design application requires an understanding of the manner in which the choice of the base

polymer, cure system, and various fillers and additives will affect the viscoelastic properties in the transition. These will be discussed in a following section. The importance of the glass-rubber transition is stressed here because it is in this frequency-temperature regime that a large number of polymeric materials will be used in acoustic applications.

In addition to temperature and frequency effects, the behavior of viscoelastic materials will also be affected by pressure. While the effects of temperature and frequency upon viscoelastic behavior are fairly well understood, the pressure dependence of viscoelasticity has not been as extensively studied. Patterson³⁰ performed tensile measurements on elastomers under a superposed hydrostatic pressure that showed the effect of increasing pressure on the Young's modulus was similar to that of decreasing temperature, with glass-like behavior being encountered above a certain transition pressure. The existence of a pressure transition in polymers is now generally accepted^{9,31,32}.

Important experimental investigations of pressure behavior of polymers include the complex bulk compliance measurements of McKinney, Marvin, and co-workers³³⁻³⁶. Others³⁷⁻³⁹ have utilized the torsional pendulum to study pressure effects on the shear behavior of a variety of a number of polymers, including elastomers. The pressure dependence of dielectric relaxation for poly(vinyl acetate) has also been investigated⁴⁰.

Ferry and Stratton⁴¹ have derived the pressure dependence of dynamic mechanical relaxations of polymers on the basis of free-volume theory in the form

$$\log a_p = \frac{(B/2.303 f_0) (P - P_0)}{f_0/k_f - (P - P_0)}, \quad (20)$$

where a_p is the ratio of relaxation times at a pressure P to the relaxation times at a reference pressure P_0 , B is a constant that is very close to one, f_0 is the fractional free volume at the reference pressure, and k_f is the isothermal compressibility of the free volume. This equation allows a procedure analogous to time-temperature superposition to be used to

superimpose measurements of viscoelastic properties of polymers performed at different pressures. Fillers and Tschoegl⁴² tested the applicability of Eq. (20) to several different types of both lightly and highly filled elastomers for measurements performed in shear and found that the lightly filled materials allowed a pressure-time superposition. By considering the bulk modulus to be linearly related to pressure, they derived a new form of Eq. (20) that describes the pressure dependence of viscoelastic relaxation and contains the WLF equation as a limiting case. For a more complete discussion of this, along with references to pertinent literature, the reader should consult Refs. 9, 42, and 43.

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CHAPTER 2

METHODS OF POLYMER CHARACTERIZATION

To completely characterize the physical and dynamic mechanical properties of an elastomer, a wide variety of measurements would have to be performed. Some of the more commonly used of these, as specified by ASTM standards, are defined in the Glossary.

Analytical procedures for the separation and identification of components of elastomeric systems are not included here. For these, the reader is referred to Part 37 of the ASTM standards and to literature sources such as the review articles of Krishnan⁴⁴ and the text by Wake et al.⁴⁵ Likewise, more esoteric topics such as small-angle light scattering, chemiluminescence, X-ray diffraction, neutron scattering, microscopy, and Raman spectroscopy, are not covered here. It is recommended that the reader consult Refs. 46 through 48 for information on these.

Another technique that is growing in importance in polymer studies is nuclear magnetic resonance (NMR) spectroscopy. No attempt will be made here to cover the subject of NMR in detail, due to space limitations and the general background of the audience at which this work is aimed. The reader who is interested in a complete treatment should consult Refs. 46 and 48 through 55. Instead, we shall briefly mention two important measurement techniques and give references to representative literature illustrating the use of NMR in polymer studies.

Two instrumental developments have occurred in recent years that have greatly extended the applicability of NMR to polymer systems. These are the development of Fourier transform techniques for NMR spectroscopy⁵⁵⁻⁵⁷, and cross-polarization magic angle spinning⁵⁸. Fourier transform NMR was important because it allowed the routine measurement of ¹³C (and other nuclei), which are of much lower natural abundance than protons, and consequently of lower sensitivity. Discussions of these may be found in the various reviews of NMR spectroscopy in polymer studies^{59,60}. Cross-

polarization magic-angle spinning spectroscopy was a useful development because it allowed the measurement of solid samples without line broadening.

Numerous reviews of the use of NMR in polymer studies have been written^{46,59-61}. The review by Cumcliffe⁶⁰ discusses techniques and instrumentation, as well as giving specific examples of structural studies where ¹³C NMR has been useful in providing new information. Cheng and Bennet⁶² have used ¹³C NMR in the analysis of ethylene-propylene polymers. Dovey^{51,63,64} has discussed applications of NMR in macromolecules. Tanaka et al.⁶⁵ have utilized proton NMR in the study of sequence distributions in styrene-butadiene copolymers. Harwood⁶⁶ has discussed the characterization of structures of diene-containing polymers by NMR. Patterson et al.⁶⁷ have used magic-angle cross polarization NMR spectroscopy to study crosslink structure in peroxide-cured polybutadiene and natural rubber.

The intent of this chapter is to very briefly describe some of the more widely used techniques for polymer characterization and studies of polymer surfaces. The discussion here includes systems for the determination of the small-strain amplitude frequency-dependent Young's and shear moduli, ultrasonic method, impedance tubes, Fourier transform infrared (IR) spectroscopy, dielectric spectroscopy, and thermal analysis.

2.1 SYSTEMS FOR THE MEASUREMENT OF YOUNG'S AND SHEAR MODULI

A large number of both "home-brew" and commercially available instruments have been devised for the measurement of dynamic mechanical properties of polymers. None of these have reached what might be called a dominant position. This is at least partially due to the fact that dynamic mechanical testing for commercial applications of rubber-like materials is often quite different from that involved in basic research on polymers. The importance of variables such as strain amplitude, frequency and temperature ranges, specimen geometry, and mode of deformation is directly related to the area of application. Some of the commonly used conventions in the field of dynamic mechanical testing of vulcanizates are summarized in ASTM D 2231-71. The discussion in the present case is restricted to

systems for the measurement of small-strain amplitude deformations in the region of linear viscoelastic behavior. A discussion of instrumentation designed for large amplitude deformation testing in automotive and other applications may be found in Ref. 68. Additionally, a brief description, along with references to pertinent literature, of a number of measurement systems can be found in the article by Medalia⁶⁹. Variable amplitude devices have also been employed in dynamic mechanical testing^{70,71}.

The purpose of this section is to provide a brief summary of several basic measurement techniques and apparatus for the determination of the frequency-dependent, low-strain amplitude Young's and shear storage moduli, as well as the loss tangent. For those who are interested in further details, Refs. 7, 9, and 14 should be consulted. Additionally, an assessment of a number of commercially available instruments and several systems developed in house at various civilian and Navy laboratories can be found in the report by Timmerman⁷².

2.1.1 Forced Vibration, Non-Resonant Techniques

A large number of instruments designed for the measurement of low-strain amplitude dynamic mechanical responses of polymers fall into the category of non-resonant forced vibration apparatus. These instruments typically measure the amplitude of both the oscillatory stress and strain and the phase angle between the stress and strain. Some of these measurements are purely mechanical, while others utilize transducer pickups and electrical analog measurements from which the complex dynamic mechanical properties can be calculated.

One of the more widely used types of this instrument, in its various incarnations, has been the progressive wave device developed by Nolle⁷³ for the measurement of the complex Young's modulus of elastomers. The basic experimental technique consists of propagating a longitudinal wave in a long, thin strip of material, which is narrow compared to an acoustic wavelength at all frequencies of measurement. A moving pickup (usually a phonograph needle) moves uniformly away from a mechanical driving element at the end of the strip. The logarithmic amplitude and relative phase of

the signal as a function of distance are recorded. The components of the storage and loss moduli are calculated from a determination of the attenuation per unit length and the wavelength. A simplified and automated version of this instrument was developed by Madigosky et al^{74,75}. It has been used extensively in material-development programs for the Navy.

A commercially available instrument that has also been widely used is the Rheovibron dynamic viscoelastimeter (currently marketed with automatic experimental control and data analysis as the Autovibron DDV-III-C, distributed by Imass, Inc., Hingham, MA). A sample specimen is subjected to a sinusoidal tensile stress by a small shaker. A strain gauge on the moving side of the instrument measures displacement, while a stress gauge on the stationary side senses force. The phase angle between stress and strain is measured as the loss tangent, while the complex modulus is determined from the measurement of dynamic force.

The instrument is normally operated at one or more of four fixed frequencies (3.5, 11, 35, and 110 Hz). To obtain extended frequency curves showing behavior of loss tangent, storage modulus, or loss modulus as a function of frequency, it is necessary to obtain data at these frequencies and over a wide temperature range and to use time/temperature superposition to construct such extended master frequency curves. As the instrument operates at small strain amplitudes, this should normally be a suitable procedure, since most materials will be in the range of linear viscoelastic behavior. A discussion of sources of common experimental errors for this instrument, as well as corrections for them, may be found in Refs. 76 through 79.

A related instrument that is manufactured by the same company and is completely automated is the Dynastat/Dynalyzer. It is capable of covering a wider frequency range, from 0.1 to 200 Hz. Additionally, it has the capability to perform both transient (creep or stress-relaxation experiments) simultaneously with dynamic experiments⁸⁰.

Rheometrics, Inc. (Piscataway, NJ) manufactures a line of instrumentation designed for rheological characterization of a large number of material types. The RMS-800 Dynamic Mechanical Spectrometer provides a measurement of the shear storage modulus and loss tangent as a function of frequency and temperature. It is also capable of performing other types of tests such as creep and recovery. The use of this instrument in studying the mechanisms and kinetics of rubber crosslinking has been described in the recently published literature⁸¹.

Another commercially available instrument that is quite versatile in its range of applications is the Metravib-04 viscoelastimeter⁸² (Gearis, International, Inc., Washington, DC). The approximate frequency range of this instrument is from 0.01 to 1000 Hz. The excitation force can be varied from 0.1 to 150 Newtons. The available temperature range is from -100°C to 1000°C. The instrument can measure the Young's modulus and loss tangent in extension and compression, as well as flexure. It can also be used to measure the shear modulus of soft polymers.

The basic experimental technique of the Metravib involves forced vibrations of a rigidly mounted sample. An electrodynamic shaker is used to harmonically excite the other end. The force applied to the sample is measured directly. The displacement of the sample is measured directly by a transducer at frequencies below 125 Hz, while the output of an accelerometer mounted in the shaker is electronically integrated to give the displacement at higher frequencies. A phasemeter is used to measure phase angle (loss tangent) between force and displacement. The instrument computes and displays the magnitude of the sample's stiffness and loss angle. These are used in conjunction with the shape factor for the specimen to compute the Young's or shear modulus, depending upon the mode of deformation. Other instruments marketed by the same company that cover different frequency ranges are the Metravib-03 and -02^{83,84}.

The Dynamic Mechanical Thermal Analyzer (manufactured by Polymer Laboratories Inc., Amherst, MA) also appears to be of the forced vibration type of instrument. It can measure the Young's modulus and loss tangent both through the flexure of a single or double cantilever beam specimen and

in tensile deformation^{85,86}. A shear sandwich geometry can be used for the measurement of the shear storage modulus and loss tangent. Discrete measurement frequencies over a range from 0.01 to 200 Hz are available. A temperature range of -150 to 300°C is available through the use of liquid nitrogen as coolant. Variable strain levels are also available. The instrument can be completely automated through the use of an optional IEE-488 interface bus and a microcomputer.

The torsional pendulum⁸⁷ is an instrument that has been widely used to measure shear modulus and loss tangent at low frequencies. The development and use of this instrument and the related torsional braid have been described by Gilham^{88,89}. Sample specimens are normally in the form of long, thin rectangular bars. One end of the specimen is clamped to a rigid support. The other end is clamped to a moment-of-inertia bar that imposes a torque on the sample when it is displaced. When the inertia member is released, the pendulum will oscillate at a natural frequency of the system. The period of oscillation will be related to the storage component of the complex shear modulus by the polar moment of inertia of the oscillating system and the sample dimensions, as well as the temperature. The decrease in amplitude of oscillation with time is due to internal damping of the sample. The rate of oscillation decrease is measured by the logarithmic decrement, which is related to the loss tangent.

The Fitzgerald transducer apparatus is another instrument for the measurement of the shear modulus that uses an electrical impedance method in which complex voltage/current ratios are measured. It is not necessary to measure absolute values of force, displacement, or velocity. The apparatus can be used on a variety of materials ranging from viscous liquids to hard solids. Its construction and operation are discussed in detail by Ferry⁹.

Measurement consists of sinusoidally shearing two disks of the sample between flat surfaces inside a cylindrical driving tube and a freely floating suspended mass. The tube and mass are radially centered by fine wires, which permits longitudinal motion. A small-amplitude, longitudinal oscillation is created by passing an alternating current through two coils

around the driving tube that are in a radial magnetic field. The floating mass moves with a much smaller amplitude, with the magnitude and phase being determined by its inertia and the elasticity of its supports. A bridge circuit is used to measure the electrical impedance of one of the driving coils while it is in motion. The mechanical impedance of the system is calculated from this measurement.

The Fitzgerald apparatus has been used over a wide frequency range, from 10 to 6000 Hz. The use of a liquid temperature bath also gives it a wide temperature range, from -60°C to 155°C . Very small stresses and deformations are normally employed in a measurement, so that the stability of the bridge balance with a change in the drive current level provides a sensitive indicator of linearity of the viscoelastic behavior of the sample.

We conclude this portion of the discussion with a brief reference to the literature sources dealing with transfer function techniques. These include the work of Pritz^{90,91} and Laird and Kingsberry⁹² on systems for the measurement of Young's modulus. Systems for the determination of shear modulus are described by Adkins⁹³, Gottenberg and Christiansen⁹⁴, and Markovitz⁹⁵. An automated torsional device for measurement of shear modulus has recently been described by Magrab⁹⁶. It has a wide frequency range and temperature control and is based upon the analysis of Gottenberg and Christiansen. Other systems have been described by Smith, Bierman, and Zitek⁹⁷, along with Ganeriwala and Rotz⁹⁸. Although numerous other examples of transfer function techniques can be found in the literature, these are mentioned due to their relative ease of implementation and the fact that they can be easily interfaced with computers and temperature-control systems.

2.1.2 Resonant Devices

Measurement techniques based on resonance methods use either longitudinal, torsional, or flexural vibrations. The theory of these measurement techniques may be found in Refs. 7, 9, 14, and 72 through 81. Longitudinal and torsional techniques are based on standing-wave phenomena.

When a system is vibrated longitudinally or torsionally at resonance, an integral number n of half wavelengths will be contained in a sample of length l . The velocity of the wave is $2lf/n$, where f is the resonant frequency of the sample. In the case of flexural vibrations, the situation is more complicated since the nodes are not at quarter points^{7,14}.

The vibrating reed^{99,100}, in various forms, has been widely used for the measurement of Young's modulus and loss tangent. In its simplest form, a thin rectangular sample is clamped at one end and forced to vibrate transversely. The vibrator is normally an electromagnetic device similar to a loudspeaker⁹⁹. A variable frequency oscillator is used to drive the vibrator. The amplitude of the free end of the reed will reach a maximum when the natural resonant frequency of the system is reached. The amplitude of vibration may be measured optically by a microscope, or by a capacitance or variable reluctance pickup. The calculations of Young's modulus and loss tangent from such measurements are discussed in Refs. 14, 99, and 100. Reference 100 describes the application of Fourier analysis to such systems.

The vibrating-reed technique is normally suitable only for materials with low losses. For high damping materials, a technique that is commonly used to measure the loss tangent is to apply a fixed displacement to the sample, release it, and measure the decay rate of the oscillation from a chart recorder output or oscilloscope display of the pickup device. The loss tangent is calculated from the decay rate.

An instrument of the Oberst beam¹⁰¹ type that has been widely used for the measurement of Young's modulus and loss tangent is the Bruel and Kjaer Complex Modulus Apparatus¹⁴. This machine, no longer a standard catalog item, can be obtained by special order. It operates by means of clamped free-flexural resonance vibrations in a metal beam coated with the polymer sample of interest. A variable-frequency sinusoidal oscillator and an electromagnetic transducer are used to induce transverse vibrations in the beam. A proximity probe is used to pick up the vibrations. A more

complete description of the theory and operation of this system can be found in the book by Read and Dean¹⁴. The instrument may also be modified to permit measurements to be made in other modes of deformation¹⁴.

The DuPont Dynamic Mechanical Analyzer^{84,102} (currently marketed as the 982) is a flexural pivot device that determines the Young's modulus and loss tangent at a single resonant frequency as a function of temperature. In this device, the modulus is proportional to the square of the natural resonant frequency of the system, and the damping is proportional to the input energy for a constant deflection level. The thickness and width of the sample can be varied to obtain the frequency variation of the modulus over a small frequency range. Master frequency curves cannot be generated with this machine because the aspect ratio cannot be varied over a wide enough range to give an accurate determination of the modulus at a sufficient range of different frequencies.

A resonance technique similar to the transfer function technique of Pritz has also been used for the dynamic mechanical testing of elastomers^{103,104}. This uses broadband excitation of a clamped-free sample bar at the fixed end with a white-noise source. The transfer function is measured, in acceleration, between the sample ends. The output signals of the accelerometers are subjected to Fast Fourier Transform (FFT) analysis, and the resultant peak amplitudes in the vicinity of the $\pi/2$ radians phase crossing points are used to calculate the Young's modulus and loss tangent at the resonant frequencies. The development of the system as used by Madigosky and Lee¹⁰³ is based on the analysis of Norris and Young¹⁰⁵. A computer interface and the use of temperature control allows time/temperature superposition to be used to construct extended master frequency curves. Semple and Thompson¹⁰⁴ recently described improvements to the solution algorithm to permit measurements at other than the resonant frequencies.

A similar resonance system^{106,107} (also based upon the analysis of Norris and Young but using discrete frequency excitation and a lock-in analyzer for measurement of the transfer function) is used at USRD for measurement of Young's modulus and loss tangent. Measurements are

ordinarily performed on two different sample lengths of the same material at the same temperature to obtain a family of curves representing Young's modulus and loss tangent as a function of temperature and frequency. Solutions to the equation of motion in the sample may be obtained at frequencies other than resonances. The system is automated, with experimental data stored on floppy disks. Time/temperature superposition and regression analysis are routinely performed to construct extended master frequency curves.

2.2 BULK AND LONGITUDINAL BULK MODULI

There are far fewer examples of determinations of polymer bulk moduli in the literature than of Young's or shear moduli. This may be due in part to the fact that such measurements are more difficult to perform experimentally. A review of measurement methods for bulk and longitudinal moduli can be found in Refs. 7, 9 and 14. In this section, we present a brief summary of some of the more commonly used methods.

2.2.1 Bulk Modulus

The pressure can be regarded as constant at any instant throughout a cavity where pressure variations are imposed on material inside the cavity if its dimensions are small compared to a wavelength of sound for any type of wave that can be propagated. A method based on this fact was developed by McKinney, Edelman, and Marvin³³ for the measurement of the bulk modulus of polymers over the 50- to 5,000-Hz frequency range. In this instrument, a piezoelectric transducer was used to insonify a polymeric specimen contained within a fluid-filled cavity whose dimensions were small compared to the acoustical wavelength for a compressional wave. A second transducer was used to detect the periodic pressure changes specified by the volume changes and bulk compliances of the cavity and its contents. The real and imaginary components, K' and K'' , of the bulk modulus can be calculated from the complex ratio of the input and output voltages, after correcting for the compliances of the oil and the container. An automated system using

the same principles was developed by Nolle and Lin¹⁰⁸ to measure the bulk compliances of polymers. A similar system¹⁰⁹, based on an acoustic coupler, is currently under development at USRD.

An acoustic pycnometer using Rayleigh scattering has been used by Holmstrom and Rudgers¹¹⁰ to measure the bulk modulus of elastomers as a function of temperature and hydrostatic pressure. The technique gave only the static modulus and has not evolved into a routine measurement method.

Another method for determining the bulk modulus that uses the solution of the inverse scattering problem has been reported by Piquette¹¹¹. This technique operates in the kHz range and gives fairly good agreement with other types of measurement systems.

2.2.2 Longitudinal Bulk Modulus

As was discussed in Chapter 1, the longitudinal bulk modulus has components of both a bulk and shear modulus. At low frequencies and moderate temperatures, it is approximately equal to the adiabatic bulk modulus. At high frequencies, it will differ considerably from the bulk modulus due to the increasing contribution of the shear component. Thus, a measurement of the longitudinal modulus and an independent measurement of the shear modulus will allow calculation of three material constants. Measurements of the longitudinal bulk modulus are normally performed through the use of an underwater acoustic impedance tube or through the use of ultrasonic devices. In this section, we will briefly discuss each of these measurement techniques.

2.2.3 Impedance Tubes

The impedance tube has been used as an acoustic measurement device for a number of years¹¹². It was originally used as a Kundt's tube using standing waves for the determination of complex specific impedance of materials for acoustic design and architecture. The adaptation of a similar type of rigid-walled, water-filled tube for measurements of

acoustic impedance was first reported by Tamm¹¹³. Similar systems were subsequently used for the evaluation of ribbed absorbing material¹¹⁴ and resonant absorbers in water¹¹⁵.

A discussion of the theory of wave propagation in such tubes can be found in the texts on acoustics by Morse¹¹⁶ and Skudrzyk¹¹⁷. The analysis of the tube is analogous to an electrical transmission line with varying terminations¹¹⁸ if it is assured that longitudinal wave propagation predominates in the tube. In such a case, the upper frequency range at which no radial modes will be found is given by $0.588 c/d$, where c is the speed of sound in the water in the tube and d is its internal diameter. The actual operating frequency range of the tube will depend upon whether it is operated in a continuous-wave mode or in a pulsed mode.

Various sample termination methods and measurement methods have been used in impedance tubes¹¹⁸⁻¹²². A consideration of some of the factors that affect the accuracy and interpretation of these results can be found in Refs. 114, 115, 118, and 123. The pulse technique itself has come to be widely accepted for the measurement of specific acoustic impedance at normal incidence, where a phase change at the reflecting surface is not required. However, the pulse technique is somewhat problematic in the difficulty of measuring the phase change in the reflected wave. Various schemes^{118,124-128} have been devised to measure acoustic impedance using pulses, but all have the disadvantage of requiring a relative comparison with a standard reflector. A significant amount of measurement time is required, since measurements must be taken at a discrete frequency (or frequencies) for both the sample and reflector. An improvement in this situation appears possible. Waterhouse¹²⁹ has discussed the applicability to measurements in water-filled tubes of transfer function techniques such as those developed by Seybert and Ross¹³⁰ and Chung and Blaser¹³¹ for making measurements in tubes containing air. A study by Corbett¹³² using a two-probe hydrophone technique indicates that such methods are feasible.

Impedance tubes are currently in operation for characterization of materials at several civilian and Navy facilities throughout the United States^{124,127,132-134}. A description of several of these can be found in

Refs. 124, 127, and 134, while a comparison study of measurements made on several of these systems can be found in Ref. 133.

We conclude this discussion of impedance tubes with a brief description of the small impedance tube facility that has been used for research purposes at USRD¹²⁴. A block diagram of the impedance tube and measurement electronics is shown in Fig. 2.1. The tube is a 6-ft-long, cylindrical, water-filled waveguide with a 2-in. i.d. and 1-in.-thick walls. The theory and construction of this tube have been previously described by Sabin¹¹⁸. Use of an external water-filled temperature-control jacket and a pneumatic pump allows measurements to be made over a temperature range from 3 to 40°C and a hydrostatic pressure up to 14 MPa.

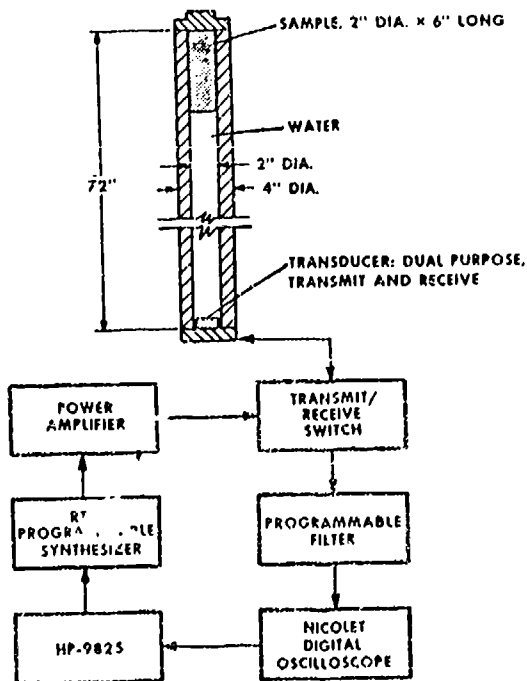


Fig. 2.1 - Block diagram of impedance tube measurement system

The tube is operated in a pulsed mode. A digital frequency synthesizer is used to provide a sinusoidal tone burst containing an integral number of cycles of the desired frequency. This is then amplified and used to drive the transducer in the tube. A coincident TTL level compatible gating pulse is used to switch the transducer to its transmit mode. After a delay corresponding to the time of flight for a pulse in the tube, a second channel on the synthesizer provides a second tone burst

delayed from the first with no jitter. This is used to trigger a digital storage oscilloscope that captures the waveform of the first pulse echo as received by the transducer. The 2 kbytes of data per channel are transferred to a minicomputer, where a discrete Fourier transform based on the Goertzel algorithm¹³⁵ is used to calculate the rms amplitude of the pulse and the phase of a given harmonic within the signal with respect to the sampling time window. This sequence is performed at each frequency of measurement (nominally 4 to 10 kHz in 1-kHz increments) for both the standard stainless-steel reflector and the sample as terminated by the reflector. To effectively decouple the transducer from the tube wall, measurements are ordinarily made at a slight hydrostatic pressure (>0.5 MPa).

For a rigidly terminated sample, the basic equation relating the experimentally determined reflection coefficient R to the complex propagation constant R is

$$(1 + R)/(1 - R) = (j\rho\omega \coth \gamma d)/(\rho' c') = Z/Z', \quad (21)$$

where ρ is the density of the sample, γ is the complex propagation constant, d is the sample length, ρ' is the density of water, ω is the angular frequency, c' is the speed of sound in water, Z is the characteristic impedance of a viscoelastic material, and Z' is the characteristic impedance of water. Sabin¹¹⁸ derived Eq. (21) by considering the impedance tube as a water-filled transmission line terminated by an elastomer-filled transmission line of length d . Alternatively, the same equation can be derived by solving the boundary-value problem for plane-wave propagation in a multi-layered medium (the thin-layer approach).

Equation (21) is normally solved by an iterative technique¹³⁶ that uses a computerized complex root finder. Values obtained for the sound speed and attenuation by this procedure can then be used to calculate the components of the longitudinal modulus from the relations

$$M' = \rho c^2 (1 - r^2)/(1 + r^2)^2, \quad (22a)$$

and

$$M'' = 2\rho C^2 r / (1 + r^2)^2, \quad (22b)$$

where $r = ac/\omega$, ρ is the density of the elastomer in kg/m^3 , C is the measured sound speed in m/sec , and a is the attenuation per unit length. Values of the storage modulus obtained by this procedure have an uncertainty of approximately 5%. It is normally found that values of the loss factor (M''/M') are very small, being on the order of 0.1 or less. However, there is considerable scatter in the loss factor values, so that observation of systematic trends in the data is difficult.

2.2.4. Ultrasonic Techniques

The propagation behavior of high-frequency viscoelastic waves in polymers provides a useful means of studying mechanical relaxation phenomena in such materials. The various experimental techniques employed are all designed to measure in some fashion or other the same two quantities: (1) the time difference Δt between two signals, and (2) the intensity difference Δi between two signals. High-frequency pulse techniques are most easily used for isotropic, homogenous solids, although they can also be employed to determine the material constants of anisotropic solids^{52,137}.

Two types of ultrasonic waves can be propagated in an unbounded, isotropic solid. These are longitudinal and shear waves. With an appropriate choice of sample geometry and measurement conditions, it is possible to propagate either or both of these in a sample. Thus, two material constants can be obtained from a single measurement technique.

Reviews of various ultrasonic measurement techniques are given in Refs. 7, 9, 14, and 138 through 140. These can be conveniently grouped into three different categories: (1) transmit-time measurements, (2) pulse-echo methods, and (3) ultrasonic interferometry. These categories can be further subdivided as to whether liquid immersion^{18,141} is used to

couple sound from the transducers into the specimen or whether the transducers are bonded directly to the specimen or any inserted delay rods^{17,142}.

A simplified illustration of a transmit-time technique is shown in Fig. 2.2. Such an apparatus was used by Ivey, Mrowca, and Guth¹⁶ for the measurement of bulk properties of several elastomers over the frequency range of 40 kHz to 10 MHz and a temperature range of -60 to 60°C. The basic experimental procedure consists of a differential measurement. A piezoelectric transducer is used to generate an ultrasonic pulse that insonifies the liquid path and the sample. The transmit time and the amplitude of the pulse received by the other transducer are measured with and without the transducer in place. The sound speed in the polymer sample and attenuation per unit length is calculated from a knowledge of the time difference, amplitude reduction, and specimen length. Corrections can be applied, if necessary, for reflections at the liquid-sample interface and attenuation in the liquid. The length of the pulses used should be such that interference effects are not produced in the received pulse. Also, the pulses used should be of sufficient length so that it can be assumed that the group velocity of the pulse is equal to the phase velocity of a continuous wave of the same frequency. Additionally, the distance between the transducers should be large enough compared to the pulse length to avoid the formation of standing waves.

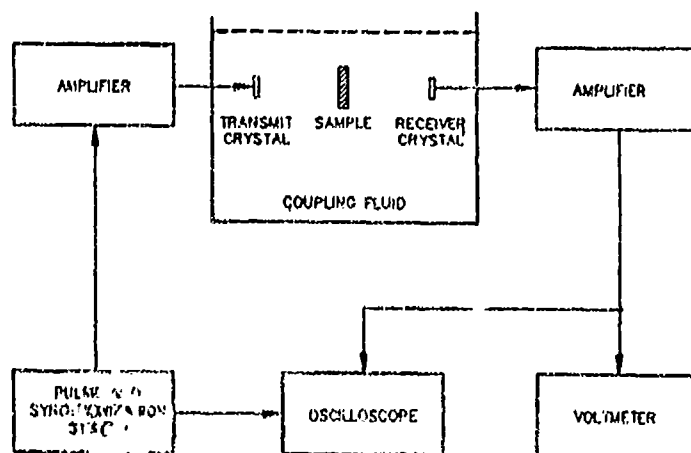


Fig. 2.2 - Block diagram of transmit-time measurement system

A version of the immersion technique that allows the determination of both longitudinal and shear wave speeds in polymers has been developed by Hartmann and Jarzynski^{141,143-145}. For measurements of shear wave speed, it uses the phenomenon of internal reflection at a critical angle in the specimen so that only a shear wave is propagated. It differs somewhat from more conventional devices using this technique^{146,147} in that the transducers are rotated with respect to the sample rather than the converse.

An example of the use of the transmit-time principle in which delay rods are used to couple the specimen and transducers can be found in the article by Nolle and Sieck¹⁷. This device was used to measure the longitudinal and shear wave speeds and attenuations of a buna-N rubber at 2, 5, and 10 MHz over a range of temperatures.

Transmit-time measurements have been used successfully on a variety of materials and have the advantage of being applicable to lossy materials. The experimental technique itself is fairly simple and requires little sample preparation. However, it is subject to end effects on the sample and requires an accurate determination of the specimen thickness and pulse transit time.

2.2.5 Pulse-Echo Methods

Examples of the pulse-echo method may be found in the systems developed by McSkimmin¹⁴⁰, May¹⁴⁸, and Papadakis¹⁴⁹. In this type of system, the transducer is bonded directly to the sample with a suitable material. The carrier frequency of the radio-frequency (rf) oscillator is set to coincide with the resonant frequency of the transducer. The pulse repetition rate of the oscillator is kept low so that the pulse train will have time to completely die away between successive pulses. The transducer serves both to transmit the signal applied from the oscillator to the sample and to receive return echoes in the interval between pulses.

Several different methods may be used to measure the round-trip time delay between echoes. A time-mark generator may be used to calibrate the delay circuits of the oscilloscope for measurement of the transmit time. A mercury

delay line was used by McSkimmin¹⁴⁰, while May¹⁴⁸ and Papadakis¹⁴⁹ used a frequency counter to measure the delay periods between echoes.

A variation of the pulse-echo method with improved sensitivity is the "sing-around" technique¹⁵⁰. This method normally employs two transducers bonded to opposite ends of the sample specimen. The signal from the receiving transducer is employed in a feedback loop that triggers the pulse generator and establishes the pulse repetition rate. Under steady-state conditions, the period of the pulse repetition frequency will be approximately equal to the delay time of the specimen. Effects of transducer-bond delays can be minimized by the use of different specimen sizes and matched transducers and bond thicknesses on both specimens. Errors due to small specimen thicknesses or low losses can be minimized by the introduction of gating circuits in the feedback loop^{151,152}. These serve to increase the effective path length of the sample.

Acoustic interferometric techniques are related to the pulse-echo method but generally allow a higher degree of accuracy for small specimens and can be used to study pressure effects. Examples of this technique are the double-gate method of Williams and Lamb¹⁵³ and the pulse-superposition method of McSkimmin^{154,155}.

These are somewhat more difficult to describe in a concise manner than the techniques covered earlier. In its simplest form, the pulse-superposition method (as developed by McSkimmin) uses a pulsed rf oscillator in addition to a cw oscillator. The repetition rate of the rf oscillator is adjusted so that an echo within a particular pulse echo train coincides exactly in time with an earlier echo in the next train. Thus, the time delay between applied pulses is equal to an integral number of round trips in the specimen. This is the $p=1$ condition as discussed by McSkimmin. When this condition is achieved, ultrasonic echoes of all orders will be summed at the transducer to produce a voltage maximum at the transducer. A constructive interference will occur every time a cw cycle in the pulse is exactly in phase with a cw cycle in the echo, so that a series of maxima will be observed as the pulse repetition frequency of the rf oscillator is varied. For complete details of these types of systems, it is recommended that the reader consult Refs. 14 and 153 through 155.

2.3 FOURIER TRANSFORM INFRARED (IR) SPECTROSCOPY

2.3.1 Basic Theory of Operation

The IR region of the electromagnetic spectrum extends from the upper end of the visible region, with a wavelength of approximately 750 nm, to the microwave region of about 400,000 nm. The most commonly used spectral region for organic molecules is from 25,000 to 160,000 nm. Infrared absorption spectra may be recorded either in wavelength or wavenumber (cm^{-1}). The wavenumber convention is widely used in the discussion of IR spectra, so that the normal range of an IR spectrum is usually about 4000 to 600 cm^{-1} . This is largely a consequence of instrument design and cost of optical components, as well as the fact that a good deal of the useful information for organic molecules is contained in this region. The energy of molecular vibrations in organic compounds corresponds to frequencies in the IR region. Only certain types of vibrational transitions with specific energy levels may take place. A discussion of the selection rules governing the number and types of transitions within a given type of molecule is beyond the scope of this work. The interested reader is referred to various texts on quantum mechanics and molecular spectroscopy for specifics^{49,156-159}. For the present discussion, it will suffice to say that only certain quantized vibrational energy levels will be allowed. A rotational fine structure will be superimposed upon the vibrational transitions, particularly in the gas phase. As a consequence of the selection rules governing the vibrational transitions, chemical functional groups will have vibrational frequencies that are characteristic for a particular functional group. The spectral region from 4000 to 600 cm^{-1} is referred to as the normal IR region and contains absorption bands due to fundamental, overtone, and combination bands.

The combination of IR interferometers, low-cost laboratory computers, and efficient algorithms for the computation of FFT has led to the development of commercially available instruments that have created something of a minor revolution in the applications of IR spectroscopy to

polymers. This is due to the fact that a Fourier transform infrared (FTIR) spectrophotometer has several advantages over a conventional dispersive instrument that arise from the basic construction and operation of an FTIR.

Complete descriptions of the theory and operation of FTIR's may be found in the books by Bell¹⁶⁰ and Griffiths and de Haseth¹⁶¹, as well as the tutorials published by companies such as Analect Instruments¹⁶² and Beckman Instruments¹⁶³. Most commercially available instruments are based upon a Michelson interferometer. A simplified illustration of such an instrument is given in Fig. 2.3. The interferometer itself consists of two perpendicular mirrors, one of which is fixed while the other is mobile at a constant velocity. A beam splitter (normally potassium bromide coated with germanium) is inserted between the two mirrors so that the incoming beam is first divided and then recombined after the introduction of a path length difference. A helium-neon laser is normally used as an internal standard to monitor the movable mirror position.

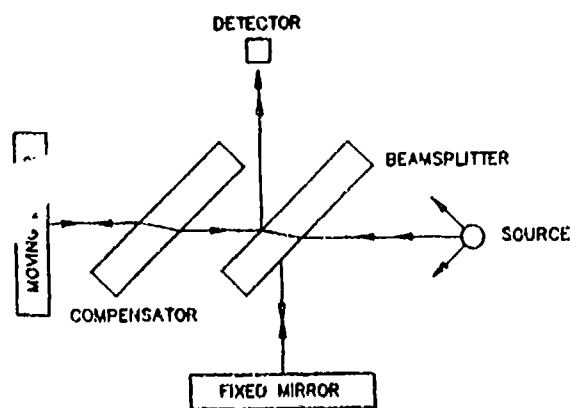


Fig. 2.3 - Block diagram of Michelson interferometer

The experimentally determined quantity is actually an interferogram that consists of a measurement of intensity of detector response as a function of mirror displacement. The resolution of the measurement is proportional to the length of the ultimate displacement of the mirror. An inverse Fourier transform is then performed, so that a spectrum that is the absorbance of the sample as a function of optical wavenumber is obtained. A discussion of factors such as beamsplitter efficiency, interferogram sampling considerations, FFT's, apodization functions, phase correction methods, and

their influence upon the resultant spectra are beyond the scope of this very cursory treatment. It is suggested that the reader consult Refs. 160 through 163 and literature cited therein if further information is desired.

The FTIR spectrometer possesses three distinct advantages over conventional dispersive instruments. The first of these is the Jacquinot¹⁶⁴, or throughput advantage. Simply stated, this arises from the fact that a conventional grating instrument is limited in its energy throughput by both entrance and exit slits and the blaze angle of the grating. The FTIR will be limited only by the beam-splitter efficiency and the size of the source aperture. This will typically give an energy advantage that is forty to fifty times greater than a dispersive system, which ultimately translates into a higher signal-to-noise ratio and better precision and accuracy in the spectra.

The second advantage is the multiplex, or Fellgett¹⁶⁵, advantage. This is a consequence of the fact that an interferometer detects and measures all wavelengths simultaneously in the same length of time as a dispersive system measures one resolution element. For the ideal case, where a high resolving power is desired, the interferometer will have a better signal-to-noise ratio than the dispersive instrument by a factor of 10^2 through 10^3 . This will be true for IR wavelengths, where the noise is usually detector noise independent of signal. For visible light, where photon noise dominates, the Fellgett advantage is lost, although interferometers still retain the throughput advantage.

The third advantage is referred to as Connes' advantage¹⁶², and is a consequence of the fact that a laser is used to track the position of the moving mirror. The wavelength accuracy of the laser allows the position and velocity of the moving mirror to be known at all times. Thus, the wavelength accuracy is consistently superior to that provided by dispersive systems. This gives much better reproducibility of spectra taken apart over a period of time.

In addition to these major advantages, the interferometric instruments are mechanically simpler, have no susceptibility to stray light, and do not cause decomposition of heat-sensitive samples due to proximity of the sample

and IR sources. The sensitivity of the FTIR to low signal levels, coupled with the fact that its rapid scanning capability makes extensive signal averaging through repeated scans feasible, makes it useful in a variety of sampling applications dealing with polymers and polymer interfaces. Recent review articles dealing with these are those by Hirst⁵⁹; Culler, Ishida, and Koenig¹⁶⁶; and Coleman and Painter¹⁶⁷.

2.3.2 Sampling Techniques

The bulk properties of polymers, as well as polymer surfaces and interfacial interactions between polymers and other types of materials, are of interest in a number of applications. These range from the need for simple identification of a polymer to mechanisms of adhesion between a coating and a substrate. Depending on what optical properties of the sample and what type of information are sought, a variety of sampling techniques may be employed. In this section, we shall summarize some of the more commonly used of these, along with references to literature describing their use in studies of polymers.

2.3.2.1 Transmission Spectroscopy

Transmission spectroscopy is a widely used method of routine IR analysis. As the name implies, it involves measuring the amount of light absorbed (or transmitted) by a sample. The sample may be in the form of a gas, liquid, or solid.

Gas samples are placed in a gas cell with an effective path length from a few centimeters up to several meters. Internal mirrors may be used to increase the effective path length of the cell. The use of gaseous samples normally requires the use of a vacuum line for storage and filling of the sample cell.

Liquid samples may be in the form of solutions or pure liquid films (neat). Neat samples are normally prepared as capillary films by placing one or two drops between two pieces of cell material [normally polished potassium chloride (KCl) or potassium

bromide (KBr)]. The thickness of the resultant film is difficult to control, giving spectra that vary in relative intensity from sample to sample. If reproducible intensities are desired, accurately sized foil spacers may be inserted between the plates to control the sample thickness.

Solid samples may be run as mulls, dispersions in KBr pellets, or as pressed or cast films. Mulls are prepared by suspending finely ground sample particles in mineral oil and recording the spectrum of the mull as a neat sample. Use of mulls is normally a technique of last resort, since not all samples can be mulled; the mineral oil displays intense carbon-hydrogen absorption bands; and it is difficult to obtain reproducible intensities from sample to sample.

The preparation of KBr pellets involves grinding a mixture of approximately 1% by weight of sample in KBr until the particles are very finely ground. The mixture is then placed in a hydraulic press and formed into a transparent disc under several tons of pressure. The disc is then mounted into a sample holder and the spectrum is recorded. The spectrum may differ from the solution spectrum due to restrictions of molecular configurations (formation of microcrystallites) or increased functional group interactions.

Pressed films are normally used for thermoplastics such as polystyrene and polypropylene. The basic sample preparation technique consists of placing a small piece of sample between two sheets of aluminum foil or Teflon and placing it in a heated press. Pressure is then applied to the material (approximately 10 tons for 30 sec). Some experimentation with temperature may be necessary to obtain satisfactory films.

The use of cast films is the technique that has been used most often for transmission studies of rubber-like materials. The films may be cast by several methods. The most commonly used one

consists of dissolving the sample in a suitable solvent, dropping the solution onto a plate of KBr, and covering it with a watch glass to let the solvent evaporate. A reasonably uniform film can be produced by this method. For viscous solutions, a microscope slide may be used to spread the solution over the crystal. Dip coating of the crystal and controlling the rate at which it is pulled from the solution will allow control of the thickness of the film.

The IR analysis of elastomers without carbon black fillers has been conducted in the past using dispersive instruments¹⁶⁸. Standard ASTM D3766 describes a procedure for analysis of pyrolysis products of several different classes of elastomers by transmission techniques.

Devlin¹⁶⁹ has successfully used transmission techniques to obtain the spectra of SBR cast films with no carbon black, and microtomed sections of SBR loaded with 50 phr of carbon black. Devlin and Folk¹⁷⁰ have also used transmission spectra of cast and microtomed samples in vulcanization studies of chlorosulfonated polyethylene. Chen *et al.*¹⁷¹ have also used this technique in studying the reversion process in sulfur-cured natural rubber.

2.3.2.2 Reflection Techniques

Reflection techniques are sampling techniques used primarily to look at material surfaces. These techniques can be broadly divided into three categories: external reflection, internal reflection, and diffuse reflection¹⁶⁶.

External reflection is used most often to study thin coatings on thin metal surfaces. The principle of external reflection can be understood with reference to Fig. 2.4a. A more complete discussion is given in Ref. 166. Briefly, the illumination of a metal surface with IR radiation causes an electric field near the

surface whose magnitude is dependent on the angle of incidence of the radiation. At normal incidence, standing waves will be found that have cancellation nodes very near the metal surface, so that no interaction with the sample occurs and no IR absorption spectrum is obtained. The same result is obtained at all angles of incidence if perpendicularly polarized light is used.

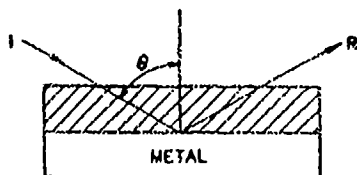


Fig. 2.4a - External reflection

The most favorable sampling is normally with an angle of incidence between 75 and 89 degrees. Grazing angle illumination and use of a polarizer in the illuminating beam may be used to achieve mono-layer sensitivity. Multiple reflections (cf. Fig. 2.4b) may be used to increase the signal level. The angle of incidence is not as critical in this case. This technique has been widely used to study polymers and surface coatings on metal substrates. This includes adsorption studies of silane coupling agents on metals¹⁷², epoxy films on iron and copper¹⁷³, and corrosion inhibitors on copper¹⁷⁴ and iron¹⁷⁵.

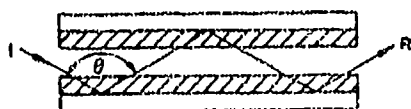


Fig. 2.4b - Multiple external reflection

Internal reflection spectroscopy is also a surface technique. It is often referred to by the name of attenuated total reflection (ATR) spectroscopy. The theory and applications of this technique are discussed in the text by Harrick¹⁷⁶.

The principle of ATR can be understood with reference to Fig. 2.4c. A sample is placed in contact with an internal reflectance element (IRE). This may be composed of thallium bromiodide, zinc selenide, germanium, or other materials. An IR beam is directed into the IRE. The IRE possesses a higher refractive index than the sample. When the angle of incidence exceeds the critical angle, total internal reflection takes place, so that the IR beam propagates down the crystal by a series of internal reflections. At each point where the beam is reflected, an evanescent wave is generated that penetrates into the sample. This wave produces the absorption spectrum.

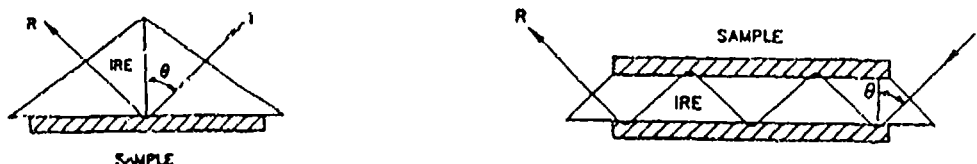


Fig. 2.4c - Attenuated total reflection

The spectra obtained by ATR are similar in appearance to those obtained by transmission techniques; however, they differ in one important aspect. This is the dependence of band intensities upon the depth of penetration of the evanescent wave into the sample. This can be expressed¹⁷⁶ as

$$d_p = \lambda_o / [2\pi\eta_1 (\sin^2 \theta - \eta_{21}^2)^{1/2}], \quad (23)$$

where d_p is the distance required for the electric field to decay to $1/e$ of its surface value, λ_o is the wavelength of the IR radiation, θ is the angle of incidence, η_1 is the refractive index of the IRE, and η_{21} is the ratio of the refractive indices of the sample and IRE.

Examination of Eq. (23) shows that the depth of penetration will reach a maximum at the critical angle of total internal reflection. The band intensities will also change significantly

across the spectral range, due to the wavelength dependence of the depth of penetration. The refractive index and angle of incidence of the IRE will also affect the depth of penetration. Thus, the greatest depth of penetration into a sample will be obtained by using an IRE with a low refractive index and a low incidence angle, such as thallium bromide with a 30-degree angle. The shallowest penetration would occur for a material with a high index of refraction and a large entrance angle.

The major experimental problem of ATR lies in ensuring good, reproducible contact between the sample and the IRE. Soft, deformable materials give good spectra, while hard samples are not readily amenable to this technique. The amount of pressure applied to compress the sample against the IRE may change the absorption spectrum. For this reason, it is difficult to obtain quantitative results with ATR. For consistent results, a special torque wrench, such as those supplied by Harrick Scientific should be used to mount samples.

The ATR technique has been applied to a number of areas of polymer science. It has been used to study the morphology and structure of polyurethanes¹⁶⁷, as well as differences between surface and bulk properties¹⁷⁷. ATR has also been used to investigate mechanisms of ozone protection in natural rubber^{178,179}. ATR may also be used to obtain spectra directly of carbon black-filled rubbers^{180,181}.

Diffuse reflectance is a technique that requires almost no sample preparation. It is based on the principle that light incident upon a powdered sample will be diffusely scattered equally in all directions. The general theory relating the sample concentrations and band intensities was developed by Kubelka and Munk^{182,183}. The sample is normally dispersed in a powdered mixture of KCl or KBr. The technique is not routinely used in the normal IR range, since the sensitivity is poor and distortion of

band shapes often occurs. However, Culler et al.¹⁸⁴ recently described the application of the technique to the study of woven glass fibers treated with coupling agents.

2.3.2.3 Photoacoustic Spectroscopy

The FTIR photoacoustic spectroscopy (FTIR-PAS) of polymers is a new variation of an old technique^{185,186}. A complete description of the photoacoustic effect is given by Rosencwaig and Gersho^{187,188}. The photoacoustic effect is based on the generation of sound when a sample in a gas-filled cell is exposed to modulated electromagnetic radiation (cf. Fig. 2.4d). The sample is placed in a sealed cell containing a carrier gas (normally helium or argon) and a sensitive microphone. Infrared radiation enters the cell through a KBr window and strikes the sample. If the IR radiation is absorbed by the sample, it will transfer this vibrational energy to the gas. Since the radiation that is absorbed by the sample is modulated light controlled by the mirror velocity of the interferometer, the heating of the sample and the gas will be periodic in nature, resulting in the formation of pressure waves in the gas. The microphone detects the pressure wave, and its amplified output is processed in the same manner as the output of a normal optical detector in an FTIR.

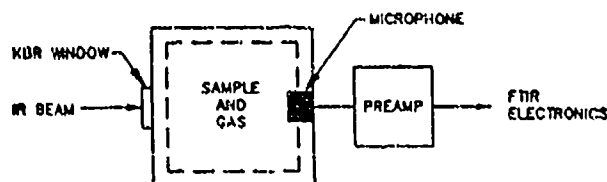


Fig. 2.4d - Photoacoustic effect

The FTIR-PAS has the experimental advantages of no sample preparation, the fact that the majority of the IR beam penetrates the sample and it is this absorption that is detected, and the fact that depth of penetration in the sample can be varied by changing the mirror velocity. In spite of these, FTIR-PAS is a

technique of last resort, due to the fact that sensitivities are very low, resulting in long sampling times. Additionally, the technique is very sensitive to the presence of water vapor.

Numerous instances of the use of FTIR-PAS can be found in the literature. For example, Vidrine¹⁸⁹ has used it to obtain spectra of a number of plastics and rubbers. Royce, Teng, and Ors¹⁹⁰ have used it to study cures in polymers. Yang et al.¹⁹¹ have discussed the applications of depth profiling of FTIR-PAS in polymer studies. Teng and Royce¹⁹² and Rockley, Davis, and Richardson¹⁹³ have discussed the quantitative aspects of FTIR-PAS.

2.4 DIELECTRIC SPECTROSCOPY

Since the initial work of Fuoss and others¹⁹⁴⁻¹⁹⁹, dielectric spectroscopy has become a useful and sensitive research tool to characterize relaxation processes in polymeric materials. For example, dielectric spectroscopy has been used to document the behavior of new polymer systems over a wide range of temperature and frequency, correlate dielectric and dynamic mechanical relaxation behavior of both new and well-known polymer systems, provide insight into molecular structural factors responsible for multiple relaxation mechanisms in polymers, and aided the interpretation of piezoelectric effects in specialty polymers such as poly(vinylidene fluoride).

No attempt will be made here to cover molecular theories of dipole relaxation. The reader is referred to Refs. 46 and 200 through 202 for these.

Most dielectric studies involve a measurement of the dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$, where ϵ' and ϵ'' are the real permittivity and loss factor, respectively. These quantities characterize the extent of electrical polarization that will be induced in a dielectric material by an electrical field. If the electrical field is an alternating one, the polarization will lag behind the field by a phase angle, δ . If the material is partly resistive, part of the stored electrical energy will be

dissipated. The stored energy corresponds to the real permittivity, ϵ' , and the dissipated energy to the dielectric loss, ϵ'' . Formally, ϵ' is analogous to the in-phase compliance, J' , that is measured in a dynamic mechanical relaxation experiment, while ϵ'' corresponds to the out-of-phase compliance, J'' . In terms of frequency and temperature behaviors, the dielectric loss more closely resembles the loss modulus in location.

Measurements have been made using both commercially available and home-made instruments. Examples of commercially available instruments are the Audrey series (Tetrahedron Assoc., San Diego, CA), and the Dielectric Thermal Analyzer (Polymer Laboratories, Amherst, MA). Examples of specially designed laboratory systems may be found in Refs. 200, 201, and 203 and in the articles by Venkataswamy, Ard, and Beatty^{204,205}.

Dielectric relaxation data for a number of polymers are tabulated in Refs. 46 and 200 through 202. Studies of elastomers, including those filled with carbon black, are documented in Refs. 200 and 201. Beatty has examined deformation effects on the dielectric relaxation behavior of polycarbonates²⁰⁴ and polyurethanes²⁰⁵. Pae and Questad²⁰³ have used dielectric spectroscopy to measure hydrostatic pressure effects on the glass transition behavior of a polyurethane material. Althouse²⁰⁶ has used dielectric techniques for quantitatively differentiating between secondary transitions and hydrogen bond disassociation in a room-temperature cured adhesive.

2.5 THERMAL ANALYSIS

In the broadest sense, thermal analysis is a group of techniques used to measure certain physically and chemically reactive properties of materials as a function of temperature. These techniques are widely used in a variety of industries for the characterization of polymers and elastomers, pharmaceuticals and other organic substances, inorganic chemicals, metals, glasses, and ceramics. The most commonly used techniques are differential scanning calorimetry (DSC), differential thermal analysis (DTA), dynamic mechanical analysis (DMA),

thermogravimetric analysis (TGA), and thermomechanical analysis (TMA). Each of these is different in its range of applications and the information that it provides.

Wunderlich²⁰⁷ has discussed the basis of thermal analysis in terms of macromolecular structure. Quantitative differential scanning calorimetry has been treated by Richardson²⁰⁸. A discussion of instrumentation has been given by Wendlandt and Gallagher²⁰⁹, who also treat commercially available instruments. Although some of the models discussed are not current ones, the discussion will illustrate the types of commercially available instrumentation. The trend in thermal analysis is toward modular, computerized units such as the DuPont 1090 or the Perkin-Elmer DSC-4 or DSC-7. A basic unit might consist of a temperature controller, computer workstation, and a differential scanning calorimeter. Additional capability can then be added by adding on a module such as a TGA system that uses the same temperature controller and computer work station.

Differential scanning calorimetry is perhaps the most widely used method of thermal analysis. Briefly, its principle of operation is based on the fact that a sample and an inert reference material that are heated at a known rate in a controlled environment will have the same increase in temperature (depending upon specific heat capacities) unless a heat-related change occurs in the sample. If the sample evolves heat, it will lead the reference in temperature, or lag if it absorbs heat. Experimentally, two types of differential scanning calorimetry instruments are commonly employed. These are the heat flux systems as used by companies such as DuPont and Mettler, and the power compensated DSC as used by Perkin-Elmer.

The basic difference in the two consists of the manner in which the enthalpy change in the sample is measured. In the heat flux system, a constantan disc that acts as part of the cell heater is also part of the temperature measurement thermocouple. A differential temperature signal is recorded and converted to energy units. In the power compensated DSC, a closed-loop electrical circuit provides differential electrical power to platinum heaters to compensate for enthalpy changes in the sample. The required power to maintain the thermal null is read out directly in

mcal/sec and is directly equivalent to the enthalpy change. A more complete discussion of differences between the two systems can be found in product literature and the review article of Wendlandt and Gallagher²⁰⁹.

Differential scanning calorimetry provides a rapid, convenient way to determine heats of transitions and temperatures of transitions in polymers. It can be used to determine the percentage of crystallinity in materials, as well as calorimetric purity. It provides a useful means of quality control. It can also be used to study reaction rates, such as the cure of systems such as epoxy resins. Shalaby²¹⁰ has reviewed the thermal characterization of thermoplastic polymers. Shalaby and Bair²¹¹ have reviewed applications to block copolymers. A comprehensive review of applications of thermal analysis to elastomer systems can be found in the work of Maurer²¹².

The DTA technique is related to DSC and provides the same qualitative information. The basic instrument consists of a heated sample block into which containers (usually quartz or glass) containing the sample and reference material are placed. Thermocouples are used to measure the temperature of both sample and reference, and indicate both the presence of transitions and the temperatures at which they take place. Differential thermal analysis is normally used for corrosive materials and as a high-temperature complement to DSC for materials such as metal alloys, ceramics, minerals, or glasses. It has also been applied to studies of elastomers²¹².

The principles of DMA were discussed earlier with regard to the Autovibron, the DuPont 982 DMA, the Polymer Laboratories DMTA, and other instruments. A further discussion of experimental techniques will not be given here. Dynamic mechanical analysis has proven very useful in studying primary and secondary relaxation mechanisms in polymers. It can also be used to evaluate the damping characteristics of various types of elastomers. It has also been used to elucidate the influence of polymer composition and temperature on the morphology of polyurethanes and other types of block copolymers²¹²⁻²¹⁵.

Thermogravimetric analysis is a measurement method that determines the weight of a sample as the sample is heated according to a predetermined temperature program. A microbalance is used to monitor the change in weight of the sample as a function of temperature and time.

The most basic application of TGA is microdistillation, which involves heating a sample at a constant rate under an inert atmosphere and recording the weight loss as a function of temperature. Most commercially available TGA's provide a way to expand the weight settings so that samples of different weights can be directly compared on a percentage basis. The microdistillation technique can be used to characterize polymers, elastomers, asphalts, and other petroleum and natural products.

Thermogravimetric analysis is also useful for thermal separation. This involves the separation of polymers or elastomer formulations into components due to differences in thermal stability or oxidizability. The separation can be performed by using a constant heating rate and switching from an inert to an oxidizing atmosphere. This technique has been particularly useful for analyzing rubber formulations^{212,216-218}. Swarin and Wims²¹⁸ have used the technique to study EPDM and NBR formulations. The technique has been used to determine both carbon black type and content in filled elastomers. Thermogravimetric analysis is routinely employed in the analysis of filled elastomer systems at the Underwater Sound Reference Detachment (USRD). An example of this is shown in Fig. 2.5 for the analysis of carbon black content of a chlorobutyl elastomer. The sample was heated under a nitrogen atmosphere to a temperature of 520°C. Oxygen was then introduced and the heating continued. The weight loss that occurs in the first part of the heating process is due to volatilization of the polymer, curing agents, and antioxidants in the formulation. The weight loss that occurs after the introduction of oxygen into the system is due to oxidation of carbon black in the system. The percentage weight change of 23.7% agrees very well in this case with the carbon black content that was specified to the rubber compounder. The residue is ash and inorganic compounds used as cure activators.

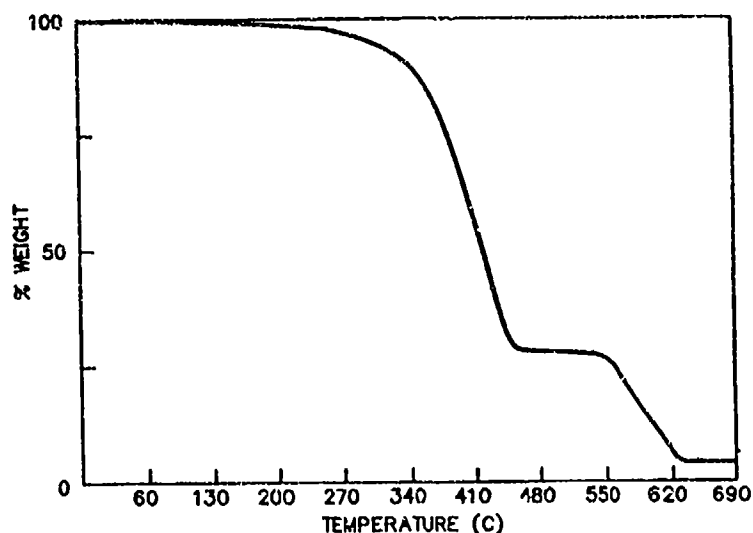


Fig. 2.6 - Thermogravimetric analysis curve for chlorobutyl elastomer

Thermomechanical analysis is a technique for monitoring the deformation of a sample subjected to a non-varying load as a function of temperature. These systems also permit thermodilatometry in which the dimensions of a sample are measured as a function of temperature as the sample is subjected to a controlled temperature program. Commercially available instruments such as the Dupont and Perkin-Elmer TMA's are based on a movable-core, linear, variable-differential transformer whose output is proportional to the displacement of the core. The sample and probe are surrounded by a Dewar assembly and a furnace. Sample temperature is monitored by a thermocouple near or in direct contact with the sample. The measured quantity is the probe displacement as a function of time or sample temperature.

Various probe configurations are available. Use of a suitable probe will allow determination of the coefficient of linear expansion and the glass transition temperature. Compressive modulus and flexural deformation and modulus can also be measured. Use of tension probes will allow extensional measurements that are very useful for characterization of fibers²¹⁰. Use of a dilatometer probe will allow a determination of the coefficient of volume expansion for a sample.

CHAPTER 3

ELASTOMERIC MATERIALS

3.1 GENERAL INFORMATION

There are a number of literature sources dealing with the selection and compounding of elastomeric materials that can provide valuable information both to those who are completely unfamiliar with rubber chemistry and those with years of experience in the area. The books by Morton and others²²⁰⁻²²³ provide good background treatments for many topics. Reference 224 is a useful compilation of information for many types of elastomers. The scientific periodical *Rubber Chemistry and Technology*, published by the American Chemical Society, describes both basic and applied research in the area of rubber chemistry. Two trade publications, *Elastomerica* and *Rubber World*, may also be worthwhile sources of information. The *Rubber World Blue Book*²²⁵ is a very useful source of information dealing with the various ingredients, as well as sources of supply, that are used in the compounding of elastomers. Manufacturers of rubber gum stocks, such as Exxon and DuPont, also provide literature for a number of their products that give helpful information on choosing cure systems, fillers, and other ingredients for particular areas of application.

3.2 COMPOUNDING OF ELASTOMERS

A complete treatment of elastomer processing would include a discussion of mixing, calendering, and extruding. Due to space limitations and the fact that this somewhat specialized area lies more within the province of the rubber compounder than the design engineer, these topics are not included here. A general discussion can be found in Refs. 220, 221, and 223. Additional articles relating to internal mixers can be found in Refs. 226 through 228. For the sake of brevity, the discussion here is limited to the various classes of ingredients that may be used in compounding an elastomer stock.

3.2.1 Choice of Gum Stock

In addition to natural rubber (NR), a large number of types of synthetic rubber have become commercially available during the past fifty years. Three standards that are useful guides to identification and selection of these are: ASTM D 1418 - Rubber and Rubber Lattices-Nomenclature, ASTM D 1566 - Standard Definition of Terms Relating to Rubber, and ASTM D 2000 - Standard Classification System for Rubber Parts in Automotive Applications.

A number of things must be considered in choosing an elastomer gum stock for a given application, so that a final choice will almost always involve some compromises. The factors to be considered include dynamic mechanical or physical service requirements, satisfactory environmental resistance, a long service lifetime, processability, ease of fabrication, and cost. These are summarized in Table 3.1.

TABLE 3.1 - FACTORS INVOLVED IN THE SELECTION OF POLYMERS[†]

Cost
Ease of Mixing
Strength Requirements
Water Permeability
Elongation Requirements
Modulus or Stiffness Requirements
Oil and Fluids Resistance Requirements
Chemical Resistance Requirements
Low Temperature Requirements
Fatigue Requirements
Moldability or Flow
Tack
Amenability to Various Cure Systems
Tear Resistance
Set or Stress Relaxation
Service Temperature
Dynamic Properties (Propagation Velocity, Hysteresis, Damping, Resilience, etc.)
Flammability

[†]After J. R. Beatty and M. L. Studebaker,
Rubber Age 107 (8), 20 (1975)

Additionally, the properties of any elastomer may be varied widely by compounding to conform to specific needs. Thus, additives may be incorporated into a formulation to improve a deficient property, improve processability, or reduce cost without significantly affecting properties. In many commercial applications where large numbers of items are to be produced and some variability in performance can be tolerated, cost may play an important factor in the selection of an elastomer gum stock. In specialty applications, cost may be a secondary factor, since availability of compounds meeting the requirements may be small.

This applications-oriented approach requires that the individual specifying a formulation know what properties need to be optimized. For a specialty area of application such as underwater acoustics, the choice of the gum stock may be dictated by static non-acoustical engineering properties, i.e., bondability, environmental resistance, or electrical resistivity. Attainment of the desired acoustical properties may then be attempted by various means. The approach to be taken requires some judgment and experience on the part of the compounder, since it is not always possible to make a precise *a priori* decision about the range of dynamic mechanical properties attainable.

Each given class of polymer will exhibit characteristic ranges of glass-to-rubber transition temperatures, loss tangent maxima and bandwidths, and magnitude and frequency bandwidth of the glassy storage modulus. Control and modification of these factors to produce a polymer with a desired set of properties may be attempted through approaches in several areas. Among the more important of these are the crosslinking system and state of cure, reinforcing and non-reinforcing fillers, and plasticizers. These, along with other classes of ingredients which will affect the service properties of elastomers, are discussed in more detail in the following sections. Another method deals with the use of blends of polymers with two or more phases in which complete or partial phase segregation exists between the phases. These include blends of different types of elastomers, block copolymers, and interpenetrating network polymers.

3.2.2 Cure Systems and Crosslinking

To convert a compounded rubber formulation into a useful end product, it must be cured in some fashion. The process of curing or vulcanization involves the application of heat to cause a reaction of the base polymer with a binding agent to form crosslinks that chemically tie together individual elastomer chains. The crosslinks are formed at statistically favorable reactive positions along the polymer chains. These are often sites of unsaturation, such as the inherent sites due to the double bonds in the skeletal structures of diene-containing elastomers or double bonds pendant to the skeletal structure resulting from cure-site monomers, such as those found in EPDM. Other types of elastomers, such as chlorobutyl, possess reactive sites that are formed by abstraction of allylic halogens. These sites are normally crosslinked²²⁹ through one or more of the following methods: (1) formation of carbon-carbon bonds through the polymer backbone, (2) insertion of multifunctional monomers such as phenolic resins between reactive sites, and (3) insertion of difunctional curatives such as sulfur or sulfur donors between reactive sites.

The cure system for an elastomer may consist of any or all of vulcanizing agents, cure activators, and cure accelerators or retardants. For many types of elastomers of practical importance, such as NR, acrylonitrile-butadiene (NBR), and butyl (IIR), cures based upon sulfur and sulfur-bearing compounds have been widely used. These include such compounds as selenium diethyl dithiocarbamate (Selenac), tellurium diethyl dithiocarbamate (Tellurac), different types of thiuram mono and disulfides, and pentamethylene thiuram hexasulfide. Sulfur-based cures normally also incorporate zinc oxide and a fatty acid as cure activators, along with some type of organic accelerator. The chemical mechanisms of sulfur-based cures are discussed in Refs. 230 and 231.

A large number of substances containing nitrogen and/or sulfur have been investigated at one time or another as cure accelerators. Organic compounds currently used as cure accelerators are generally thiazole types,

sulfenamide types, dithiocarbamate types, and thiuram types. For a discussion of the properties of these compounds, the reader should consult Refs. 220 through 225.

Several different types of compounds may function as accelerator activators. Zinc oxide is necessary to activate the types of cure activators previously mentioned. It is normally added in 3 to 5 parts by weight on the rubber, and should be low in lead content. A fatty carboxylic acid, such as stearic, is a useful cure accelerator. The fatty acid is believed to react with the zinc oxide present to form a rubber-soluble zinc soap under curing conditions²³⁰. This soap, in turn, reacts with the accelerator to allow it to exert its full effect.

Certain alkaline substances [such as litharge (PbO) and magnesia (MgO)] and certain types of calcium carbonates, furnace blacks, and amines will act to accelerate vulcanization. Materials of an acidic nature, if present in sufficient quantity, will tend to retard curing. Thus, benzoic and salicylic acids and N-nitroso diphenylamine are used for scorch control in some hot-processing stocks.

3.2.3 Effects of Crosslinking

The physical and dynamic mechanical properties of lightly crosslinked properties will be influenced by both crosslink type and density. Crosslink type refers to the linkage type (i.e., carbon-carbon, carbon-sulfur-carbon, carbon-sulfur-sulfur-carbon), while crosslink density refers to the moles of crosslinked basic units per weight unit of polymer.

An idealized illustration²³² of the effects of crosslinking on an elastomer is shown in Fig. 3.1. It can be seen that the extent of crosslinking will be reflected in the static modulus, hardness, and the dynamic Young's and shear moduli. Bulk deformation properties will not normally be affected by entanglements and crosslinks⁹. Additionally, tensile and tear strengths will generally tend to increase with increased crosslink density at low levels of crosslinking. Above a certain crosslink density, however, they tend to decrease.

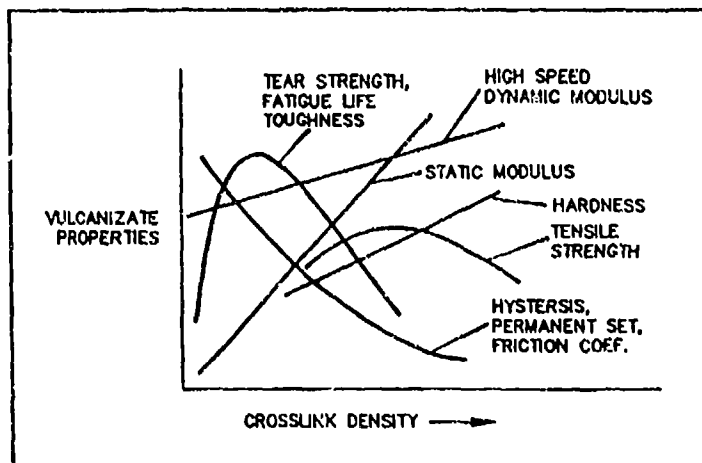


Fig. 3.1 - Effect of crosslink density on vulcanizate properties (after Refs. 229 and 232)

Increasing the degree of crosslinking will also tend to increase the glass-to-rubber transition temperature so that at a given temperature, the transition region in the dynamic modulus curve will occur at a lower region in the frequency spectrum. Also, the thermal history of a material during cure should be closely monitored, since its properties will often depend critically upon the details of any heat treatments it receives during curing and bonding.

3.2.4 Fillers

A technique that provides an even wider latitude in adjustment of elastomer properties is the use of fillers. For many service applications, it is necessary to incorporate into the rubber relatively large amounts of reinforcing material to increase its hardness, stiffness, tensile strength, creep resistance, and resistance to abrasion and tear. These materials also have a pronounced effect upon the dynamic mechanical properties of elastomers. These filler materials include various carbon blacks, zinc oxide, fine-particle calcium carbonates, hard clays, and hydrated silicon compounds such as silicon dioxide.

Because carbon black is such an important class of filler for elastomers and because such a large amount of research has been done in this area, the discussion of fillers here is restricted to this category. Those who are interested in work dealing with mineral fillers should consult Refs. 75, 223, and 233 through 235.

A number of standards that define conditions with regard to carbon black may be found in part 37 of the ASTM standards. Among the more important of these are: D 1765-82 - Classification System for Carbon Blacks Used in Rubber Products, D 3053-81a - Definition of Terms Relating to Carbon Black, D1510 - Testing Carbon Black-Iodine Absorption Number, D 1512-80a - Testing Carbon Black-pH Value, D 2263-82 - Testing Rubber Compounds-Dispersion of Carbon Black, D 3037-81 - Tests for Carbon Black-Surface Area By Nitrogen Adsorption, and D 3493 - Testing Carbon Black-Dibutyl Phthalate Absorption Number of Compressed Sample.

Both the physical and viscoelastic properties of elastomers will be affected by the addition of carbon black fillers. The degree of effectiveness of a carbon black will depend primarily upon four factors: (1) particle size of the carbon black, (2) structure of the carbon black, (3) surface chemistry of the carbon black, and (4) degree of dispersion of the carbon black.

The effect of surface chemistry is reflected primarily in the influence of pH and surface area upon the cure rate of elastomers. Finer sized blacks of greater surface area tend to increase the rate of cure. This may be due at least in part to the fact that these materials generate more heat upon mixing that subsequently leads to shorter scorch times. Acidic channel blacks will tend to retard cure, while alkaline furnace blacks will act as cure accelerators.

Good dispersion of the carbon black is essential if the properties of the rubber are to be optimized. Dispersion of carbon black has been categorized in terms^{236,237} of agglomeration, networking, and polymer phase distribution. The latter category refers to blends of elastomers^{238,239} and represents a means by which the phase continuity and location of the black can be varied by alteration of the blend proportions or mixing procedure to control the physical and dynamic mechanical properties of the polymer. Agglomeration refers to the formation of large clusters of carbon aggregates. These agglomerates are further classified as hard or soft agglomerates, depending on the extent to which they have been penetrated by the polymer during mixing. Hard agglomerates have the most

detrimental effects upon physical properties²³⁶. Networking represents the tendency of the black to form chain-like three-dimensional aggregates of carbon black particles in the rubber mix after the black has been dispersed. Networking is more prevalent at higher loadings of high-structure blacks⁶⁹ and plays an important role in the low strain dynamic mechanical properties of elastomers.

Historically, the most frequently applied method of examination for carbon black dispersion has been to examine the cut or torn surface of the vulcanizate. If the surface is dull and rough, poor dispersion and the presence of agglomerates is indicated. A smooth and glossy surface indicates good dispersion²⁴⁰⁻²⁴³. However, these procedures are difficult to quantify. More precise procedures^{244,245} based upon stylus-type microroughness testers have been reported. These are normally calibrated for different rubber systems by light microscope methods (ASTM D 2263, Method B). Laser optical scanning procedures²⁴⁶ have also been used to obtain surface roughness measurements that can be related to carbon black dispersion.

Measurements of electrical resistivity^{245,247} have also been used as indicators of carbon black dispersion. It has been found that resistivity increases with improved dispersion for a given compound. The technique works best²⁴⁵ for small and intermediate sized blacks at intermediate loadings.

Physical properties such as hardness, tear strength, tensile strength, and static modulus will all be influenced by both the particle size and loading of a given type of black in a particular compound. An illustration of this is given in Fig. 3.2 for a Neoprene GRT compound¹⁰⁷, showing that the shore hardness of this compound increases in an approximately linear fashion with increasing loading of the same black. It is also found that increasing the loading of a given type of black will increase the tear and tensile strengths, while decreasing the ultimate elongation. A qualitatively similar effect is obtained by going to smaller particle size blacks.

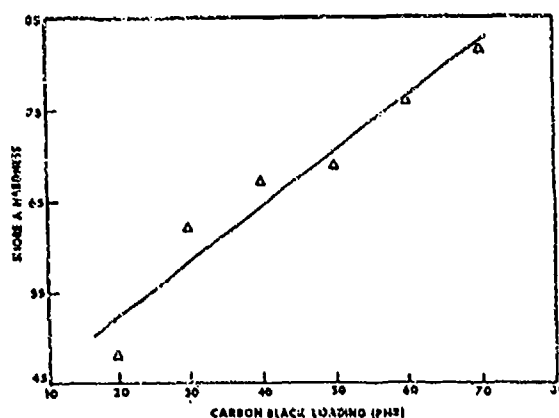


Fig. 3.2 - Plot of Shore A hardness vs carbon black loading for Neoprene GRT compound reinforced with N660 black

The dynamic mechanical properties of carbon black-filled elastomers will be greatly altered by the incorporation of carbon black fillers. The viscoelastic properties of these materials are quite sensitive to the strain history and strain amplitude imposed upon them^{69,70,199,248-252} so that, strictly speaking, a rubber containing carbon black or other reinforcing filler does not have a unique value of modulus or loss tangent at any given frequency or temperature. The dynamic mechanical properties of such an elastomer will exhibit the behavior depicted in Fig. 3.3 as a function of strain amplitude. Also, a comparison of the dynamic modulus and loss tangent due to addition of a given black at different degrees of loading in the same elastomer contains the implicit assumption of duplication of degree of dispersion and crosslinking. For this assumption to be valid, careful attention must be paid to mixing and cure conditions.

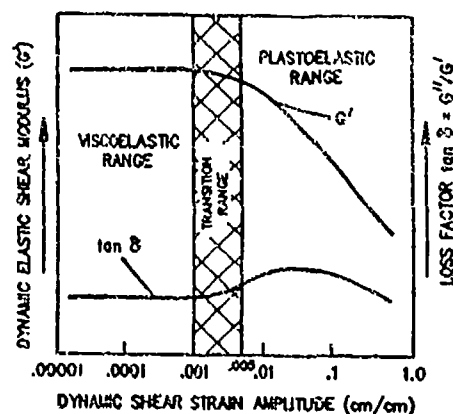


Fig. 3.3 - Effect of dynamic shear strain on the dynamic modulus and loss factor of a typical elastomer (after Ref. 70)

At low frequencies at a constant temperature (the rubbery region) increased loading of carbon black will cause an increase in both the storage and loss moduli. As the polymer goes through the transition

region, the loss modulus will pass through a maximum. The rates at which the storage and loss moduli change will determine whether or not addition of carbon black causes an increase in hysteresis. For some materials^{107,249,249} it has been found that increased loading of carbon black causes an increase in the loss tangent at low frequencies. Most materials tend to exhibit a lowered loss tangent in the transition region as the loading of carbon black is increased, while the storage modulus tends to increase uniformly across the entire frequency range, as shown in Fig. 3.4. Additionally, increasing the loading of carbon black causes a broadening of the loss tangent peak and a decrease at a constant reference temperature in the frequency at which the rapid increase in the slopes of the modulus-frequency and loss tangent-frequency curves occur.

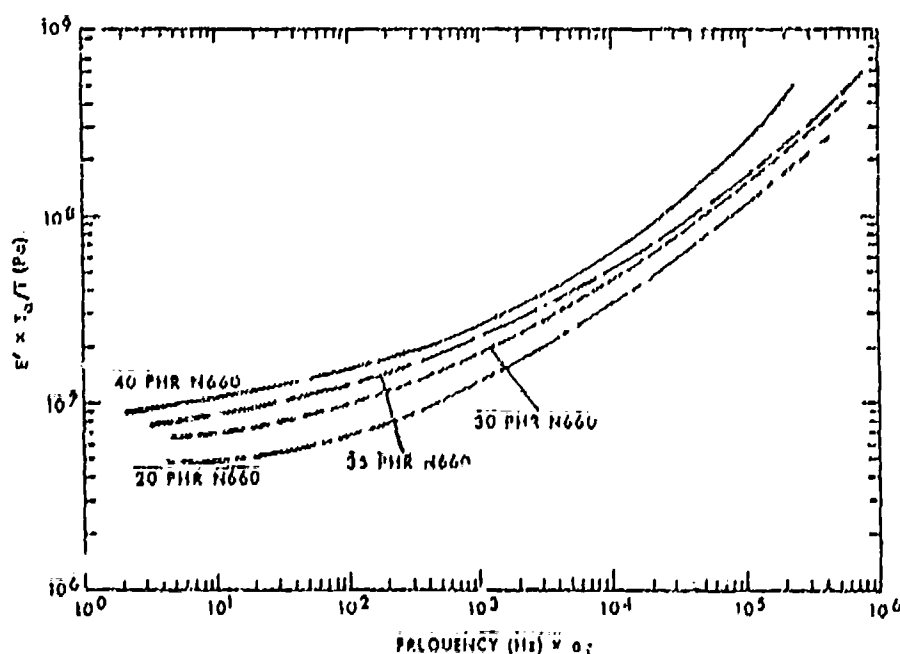


Fig. 3.4 - Plot of storage Young's modulus vs reduced frequency at 200.16K for Neoprene WRT at various loadings of N660 black (phr = parts per hundred of rubber)

Loss mechanisms for carbon-black-filled elastomers are considered to arise from molecular friction in the gum phase, interactions at the carbon black-elastomer interface, and interactions between agglomerates of carbon black and occluded elastomer or their spheres on the overall filled elastomer undergo deformation²⁴⁸. Various models have been proposed for

the nature of the interaction of the rubber matrix and the carbon black itself. It has been suggested²⁴⁹ that the polymer chain of the elastomer forms a chemical bond with the carbon black so that it is rigidly attached to a surface site on the carbon black, with only a limited loss attributable to surface effects. Others^{251,252} have proposed that dewetting of the polymeric matrix from included solids occurs, so that rubber molecules are able to relieve stress concentrations in the vulcanized elastomer by slippage along the carbon black surface. The best available evidence to date^{70,199,248-250,253} suggests that a major loss mechanism, particularly at high strain amplitudes, is the breakdown of a three-dimensional network of aggregates.

Previous studies^{69,70,107,199,248-250,254} have amply demonstrated that the dynamic properties of carbon black-reinforced elastomers are dependent upon the strain amplitude imposed upon them. At ordinary loadings of carbon black, a three-dimensional network of carbon black aggregates is formed in which the aggregates are held in contact by van der Waals forces. The nature of the interaction of the black will be influenced by both the structure and particle size of the black^{199,248-250}. The effect of the individual aggregate is a function of the structure of the carbon black, and appears to play an important role in the dynamic mechanical properties of filled elastomers at high-strain amplitudes. The effect of the network is a function of the particle size. Small strain amplitude measurements have shown^{75,107,255,256} that the longitudinal modulus, as well as the Young's and shear storage moduli, tends to increase with decreasing particle size of the black. This is illustrated for a Neoprene GRT in Figs. 3.5 and 3.6.

It has also been found that larger sized blacks of lower surface activity tend to give increased $\tan \delta$ values. In the case of carbon blacks of widely varying particle sizes, it has been observed^{76,107} that the maxima in $\tan \delta$ versus frequency curves at a fixed temperature are sharper and of greater magnitude for the less reinforcing, larger sized black. The greater temperature and frequency sensitivities of the viscoelastic responses of elastomers filled with the larger sized blacks is presumably due to a greater volume of occluded rubber in the elastomer reinforced with

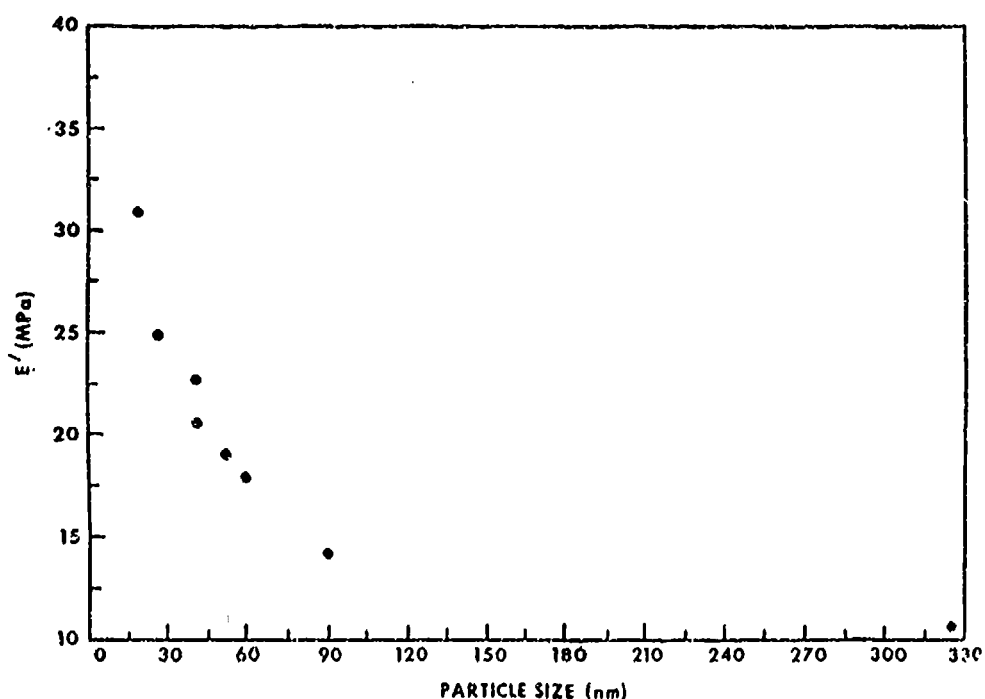


Fig. 3.5 - Plot of storage Young's modulus vs carbon black particle size at 80 parts loading for Neoprene GRT formulations at 1000 Hz and 293.15K

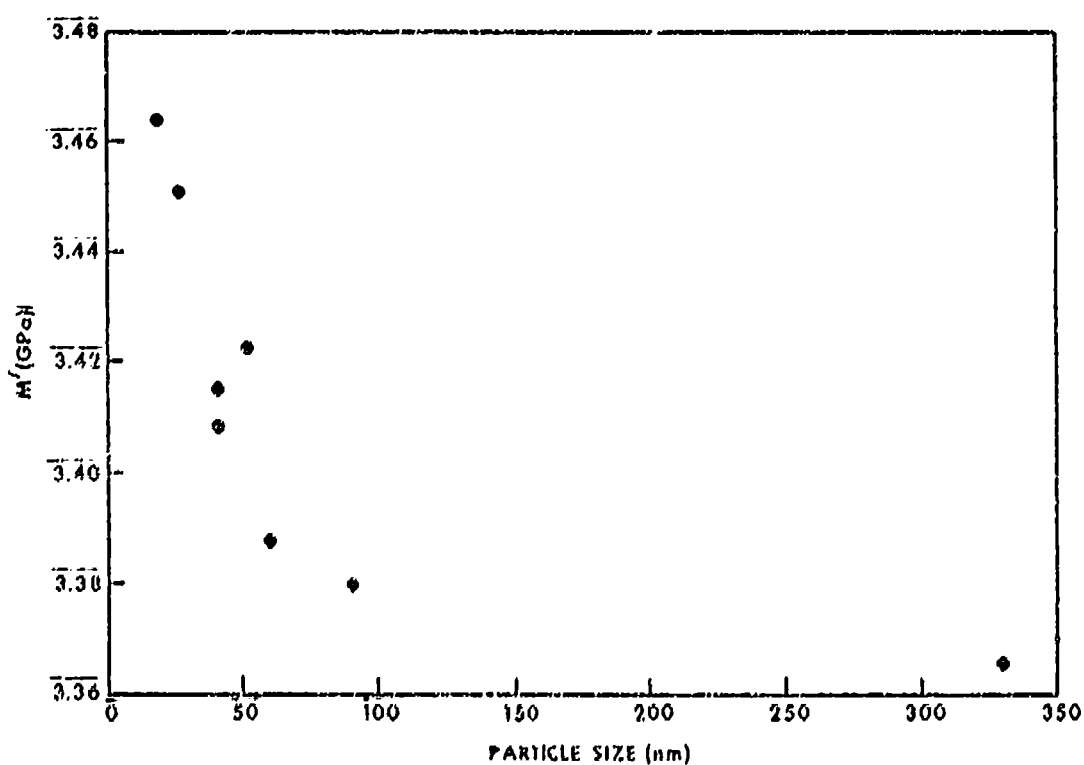


Fig. 3.6 - Plot of longitudinal modulus vs carbon black particle size at 80 parts loading for Neoprene GRT formulations at 1.8 MHz and 293.15K

the smaller sized black and different degrees of stress distribution under different degrees of aggregation. Qualitatively, one would expect the effect of using a smaller size black to be the same as that of increasing the degree of crosslinking or the loading of black; i.e., an increase in T_g (the glass transition temperature). However, this effect is minor compared to that obtained through the use of plasticizers⁷¹.

In summary, it can be said that carbon black-reinforced elastomers can be viewed qualitatively as a combination of a crosslinked polymer network with a network of carbon black particles. The viscoelastic properties of these systems are much more complicated than those of simple gum phases, with a strong dependence upon strain history and strain amplitude. Lightly crosslinked polymers normally appear to exhibit linear viscoelastic behavior under small strain amplitudes and obey the principle of time/temperature superposition. The exact nature of the interaction of carbon black will depend upon the elastomer itself, the degree of crosslinking, and the size and structure of the black. To obtain consistent results with a given type of black within a polymer system, careful attention must be paid to mixing and cure conditions.

3.2.5 Plasticizers, Processing Aids, and Softeners

Various materials are usually added to raw rubber stocks to facilitate mechanical breakdown and ease of processing during compounding. These are softeners, processing aids, plasticizers, and extenders. The distinction between some of these materials is nebulous. Typically, oils added in small amounts tend to act as softeners, while larger amounts are used as extenders. Petroleum oils find extensive use as softeners and plasticizers. The chemical composition of these oils is quite complex.

Plasticizers are useful in several aspects of compounding. They permit rapid incorporation of fillers and other ingredients during the mixing cycle. They reduce internal friction in calendaring and extrusion, thereby helping to minimize scorch. Plasticizers and softeners are also useful in compounding for applications that may require low modulus and hardness. These materials are usually organic, non-polymeric or low molecular weight

polymeric, and weakly polar organic compounds with low glass-transition temperatures and high boiling points. The high boiling point is necessary to prevent loss by volatilization.

The plasticizer functions by a solvating action^{71,257-260}. The individual plasticizer molecules distribute themselves through the polymer network and separate the polymer chains. To be effective, the plasticizer must be compatible with the polymers to which it is added, and is useful only in amorphous polymers or in the amorphous region of partially crystalline polymers. Additionally, it should have a low viscosity and a large free volume, as the solvating action will contribute to the total free volume of the plasticized polymer and increase the effective volume available for each polymer chain to move. The net effect of plasticization will normally be to lower the glass transition temperature and broaden the transition region^{71,257,258,260,261}.

3.2.6 Antidegradants

Elastomeric materials tend to undergo changes in properties with the passage of time. Oxidation by atmospheric oxygen is a major cause. The extent of aging will be influenced by a number of internal and external factors. The internal factors include the type of elastomer, the cure system, and antidegradants. The article by Parks and Spacht²⁶² is an excellent discussion of the use of antioxidants in rubber compounds, with a list of the general classes of antidegradants and their properties and uses.

The chemical nature of the elastomer itself will influence, to a certain extent, the aging characteristics of a rubber article. The more highly saturated polymers such as IIR and ethylene propylene diene (EPDM) exhibit better resistance to aging than do elastomers with more unsaturation, such as NR and styrene-butadiene (SBR). This is probably related to the fact that oxidation of rubber is a free-radical process.

The elastomer must be protected both during storage and processing and after vulcanization. Materials used for protection during storage and processing are referred to as stabilizers. Stabilizers may be destroyed or rendered ineffective during vulcanization; thus, they do not always serve as antioxidants in the vulcanized product. The minimum amount of stabilizer is normally added, with the assumption that additional antioxidants will be added during compounding to give the desired aging characteristics. Proper stabilization is important because oxidative degradation of the polymer during storage cannot be compensated for through the use of additional antioxidants during compounding.

There are a number of factors external to the polymer itself that affect the aging of elastomers. These factors are heat, oxygen, fatigue, metal catalysts, and ozone.

Generally, heat is an important factor in rubber aging in cases where elevated temperatures are routinely encountered. A number of tests (ASTM's D 573-67, D 865-62, and D 1870-68) are useful in studying the effects of heat on rubber in accelerated aging. The accelerated tests are helpful in that they show general trends. In many cases, however, it is difficult to correlate results between natural and accelerated aging.

The effect of oxygen on an elastomer will depend on the type of rubber and the aging conditions to which it is subjected. In general, two competing processes will take place. These are chain scission and crosslinking. Chain scission, as the name implies, results in the breaking of bonds. The net effect of chain scission is a reduction in tensile strength. Natural and butyl rubbers and polyisoprene are more susceptible than other types of rubbers to chain scission.

Crosslinking results in the formation of new bonds as a result of sites of unsaturation that are present in the elastomer. Crosslinking typically results in a loss of elasticity that is characterized by an increase in modulus or hardness or a decrease in elongation. Polychloroprene (neoprene) and butadiene rubbers such as polybutadiene, SBR, and NBR are most susceptible to crosslinking. Prevention of hardening due to

crosslinking is difficult, as antioxidants have little effect in protecting butadiene rubbers. P-phenylenediamines appear to offer some protection^{262,263}.

Repeated extensive, compressive, and bending forces on an elastomer may lead to a serious reduction in its useful service life (ASTM's D 395-78, D 430-73, D 623-78, and D 1052-55). The prevention of cracking during flexing is an important use of antioxidants in compounding. One of the most important types of fatigue failure, flex cracking, involves both a mechanical fatigue and a heat build up during flexure that acts to accelerate oxidation. For this reason, antioxidants for heat resistance are also used to prevent dynamic fatigue. The N-alkyl-N'-phenyl-p-phenylenediamines are among the best flex-cracking antioxidants²⁶², while N-nitrosoamines also offer effective protection²⁶⁴. Recommended procedures for testing the effects of fatigue on elastomers can be found in ASTM's D 430-75 and D 623-67.

Trace amounts of transition metal ions such as copper, iron, and manganese may have an adverse effect upon the service life of an elastomer. This is due to a catalytic effect these ions exert on the free radical generation in the oxidative decomposition of rubber^{223,262}. These metals may be present in the elastomer itself (as trace impurities in mineral fillers) or be introduced by processing equipment. Chelating agents are normally used to protect raw polymers but have not found extensive use in compounded stocks. The p-phenylenediamines, commonly used antioxidants, are also effective chelating agents. The process of vulcanization itself also affords some protection, as the metal ions are converted into insoluble salts. Reference 223 gives chemical tests for the detection of copper and manganese in elastomers.

Exposure of an elastomer to light in the ultraviolet wavelength region may lead to deterioration by catalyzing the auto-oxidation of the rubber²⁶². White or light-colored rubbers may discolor to an objectionable degree or develop a brittle surface layer that will shatter upon flexing. This condition is known as crazing. It can be prevented by adding carbon black or ultraviolet (UV) absorbing materials to the rubber.

Since crazing is a surface effect, the UV absorber must bloom to the surface to be effective. Materials such as nickel dithiocarbamate and 0-hydroxybenzophenone derivatives have been used as UV absorbers^{262,265}. Certain waxy materials (such as paraffin, syncera wax, ozokerite, and others) are often added in excess of their solubility in rubber. These materials will then migrate to the surface of the rubber after vulcanization, and the resulting film will protect the rubber from crazing.

A light discoloration test for light-colored rubbers using a source of UV radiation is contained in ASTM D 1148-77. ASTM D 750-68 describes equipment procedures for accelerated aging tests using sample exposure to calibrated light sources.

The effect of ozone upon rubbers is also typically a surface effect. The mechanism of the reaction of ozone with rubbers is believed to proceed through ozonolysis^{262,265}. The ozonide intermediates decompose to cause chain scission, resulting in the formation of cracks in a stressed rubber. The characteristic feature of ozone cracking is that the cracks are at right angles to the direction of strain. In unstressed rubbers, ozonolysis will give a bloom-like appearance called frosting.

The formation of cracks is dependent on the degree of elongation of the rubber. The exact degree of elongation necessary for cracks to begin forming will depend on the type of rubber and compounding ingredients, but is normally in the range of 5 to 10%. At a high degree of elongation, the cracks become more numerous and are smaller. At a low elongation, large, deep cracks are found. It is these larger cracks that typically lead to rubber failure²⁶².

The type of rubber will also affect cracking. Natural rubber forms many fine cracks, while SBR forms large cracks. Neoprene and butyl rubbers display much better ozone resistance than SBR or NR's. Protection of rubbers against ozone often involves surface coatings or waxes that bloom to the surface of the rubber to form a protective film. Certain combinations of polymers also give good ozone resistance, such as nitrile

rubbers with poly(vinyl chloride)²⁶². Recommended procedures for evaluation of ozone attacks on elastomers are given in ASTM's D 1149-77, D 1171-68, and D 3395-75.

For a more detailed discussion of aging in elastomers, the reader should consult Refs. 221 through 223 and 262. Reference 224 contains a useful compilation of the results from aging tests on different types of elastomeric materials. Information on commercial antioxidants and suppliers can be found in the *Rubber World Blue Book*²²⁵, as well as Refs. 222 and 223. Table 3.2 summarizes the weathering characteristics of various types of elastomers.

TABLE 3.2 - AGING PROPERTIES OF DIFFERENT TYPES OF ELASTOMERS

Elastomer Designation	Ozone Resistance	Sunlight Resistance	Weather Resistance
Butadiene (BR)	Fair*	Fair	Fair*
Butyl (IIR)	Good	Good	Excellent
Chlorosulfonated Polyethylene (CSM)	Excellent	Excellent	Excellent
Ethylene Propylene Diene (EPDM)	Excellent	Excellent	Excellent
Fluorocarbon (CFM)	Excellent	Excellent	Excellent
Natural Rubber (NR)	Fair*	Fair	Fair
Neoprene Rubber (CR)	Excellent*	Excellent	Good
Nitrile Rubber (NBR)	Fair	Fair	Fair
Polysulfide Rubber (T)	Excellent	Excellent	Excellent
Silicone Rubber (MQ)	Excellent	Good	Good
Styrene-Butadiene (SBR)	Fair*	Fair*	Fair
Urethanes (U)	Excellent	Variable*	Excellent

*Requires special compounding

3.3 VULCANIZATION AND MOLDING

To convert most natural and synthetic rubbers to a finished product, it is necessary to apply heat in some form or other. This process of vulcanization may be accomplished in a number of ways, depending upon the

size and structure of the finished product and the elastomer being processed. These include autoclave vulcanization in open steam, autoclave vulcanization under water, fluid-bed vulcanization for extruded products, and press vulcanization. References 222 and 223 discuss all of these methods. The use of polymeric materials in acoustical systems will often involve the molding of specially shaped articles by compression, transfer, or injection molding, so that the discussion in this work is directed towards press curing.

In order for the finished rubber product to exhibit the desired chemical and physical properties, it must reach the proper state of cure. Properties such as tear and abrasion resistances, creep cracking resistance, hardness, flexing properties, modulus, and others will all be affected by the state of cure.

To determine what is an "optimum" cure, it is customary to make a series of cures (usually for different lengths of time at the same temperature) and to measure the physical properties of the vulcanized product. Various parameters (such as maximum tensile strength, tensile modulus, and ultimate elongation) have been used at one time or other as criteria for judgment of optimum cure. The modulus is now generally used.

To lessen the time and effort involved in experiments to evaluate the above quantities, a number of instruments have been developed that continuously measure the characteristics of an elastomer while it is being vulcanized. Two of the more widely used of these are the Monsanto Oscillating Disk Rheometer (ASTM D 2084-79) and the Mooney Viscometer (ASTM D 1646-80).

The Monsanto Oscillating Disk Rheometer is designed to monitor the curing characteristics as a function of time of a single rubber specimen that is heated and maintained at a constant temperature and pressure during vulcanization. The vulcanizable elastomer is contained in a heated cavity with a conical disk imbedded in it. The sinusoidal oscillation of this disk exerts a shear strain upon the elastomer. The torque necessary to oscillate this disk is directly proportional to the shear modulus of the

elastomer. The resistance of the rubber to the oscillating disk is measured by a strain transducer on the torque arm and is plotted automatically to yield a curve of torque versus cure time. A complete description of the Oscillating Disk Rheometer and its operation is contained in ASTM D 2084-79, along with recommended procedures for determining the time to optimum cure for an elastomer sample. The graph obtained from a rheometer exhibits such parameters as minimum torque, scorch safety, cure rate, and maximum torque. This information is desirable for repeatability of cure from one sample of elastomer to the next. The use of the Oscillating Disk Rheometer in statistical process control is discussed in Ref. 266.

The Mooney Viscometer is a shearing disk viscometer that may be used as a standard method for determining the viscosity of elastomer materials in the raw or compounded state and for determining the cure characteristics of such materials. The rubber is contained under pressure in a shallow cylindrical cavity. A disk rotating in the cavity provides the shearing action. The operation of this machine and recommended test procedures are described in ASTM D 1646-80.

The viscosity of elastomers (vulcanizable or unvulcanizable) may be determined over a range of temperature by using an arbitrary set of units under standardized conditions. To determine the cure characteristics, the viscosity of vulcanizable elastomers is recorded during heating at a constant temperature. Minimum viscosity and rate of change of viscosity in specified amounts are used as arbitrary measures of the start and rate of cure. The method cannot be used to study complete vulcanization because it requires the continuous rotation of the disk inside the cavity.

Another instrument used to measure the cure characteristics of elastomers is the Rheometrics Dynamic Mechanical Spectrometer^{81,171,267,268} (cf. Chapter 2). Hill⁸¹ has studied the behavior of a silicone elastomer at different cure temperatures using this device, while Chen et al.¹⁷¹ have used it to study the reversion process in sulfur-cured NR. Unlike oscillating disk rheometers, the dynamic mechanical spectrometer allows both a complete rheological profile during the cure cycle as well as the

moduli and viscosity of the cured compound. The measurements can be made at different frequencies and strain levels at different temperatures. The dynamic mechanical spectrometer provides the absolute value of the complex shear modulus, G^* , the storage and loss modulus, the loss tangent, the complex viscosity, η^* , and torque. The machine should prove to be very useful for monitoring cure cycles, studying reaction kinetics, and process optimization.

Press curing of an elastomer requires that the compound to be cured flow properly without scorching before the desired shape is reached. The elastomer should also be easily removable from the mold after cure. This requires a proper mold design and the use of mold lubrication.

A commonly encountered problem is porosity in thick articles. This is generally caused by undercuring or insufficient external pressure during the initial portion of the cure. The thickest portion in the cross section of the finished article should be examined for porosity, and the cure cycle should be correspondingly adjusted if it is found. Problems with porosity can usually be solved by the use of a more suitable cure accelerator. If problems with porosity suddenly develop with elastomers that have previously been satisfactory, then moisture in the filling agents or improper dispersion of sulfur or accelerators in the compound should be suspected.

Trapped air inside the finished product is a common fault in many press cured articles. It may be caused by improper mold design, using an elastomer that is too soft, or improper filling of the mold before the cure cycle is started. Often, a well designed injection or transfer mold will solve this problem.

Compression molding is the simplest of the rubber molding processes. The mold is a simple flash type with tapering pins for registering the two halves of the mold. A simplified example is shown in Fig. 3.7a. An excess of uncured, room-temperature elastomer is placed in the cavity (or cavities) of the mold. The top is put into place, and the two halves of the mold are squeezed together between the two heated platens of a press.

As the rubber reaches its softening temperature, it begins to flow and assume the shape of the mold cavity. The excess elastomer flows out into the overflow grooves of the mold and is called the flash. The mold should be designed so that the placement of the flash does not affect the performance of the finished product. The rubber begins to cure as soon as it reaches its vulcanization temperature (often near 150°C for many compounded elastomers). The mold should then be left in the press, under pressure, for the length of time necessary for optimum cure of the elastomer.

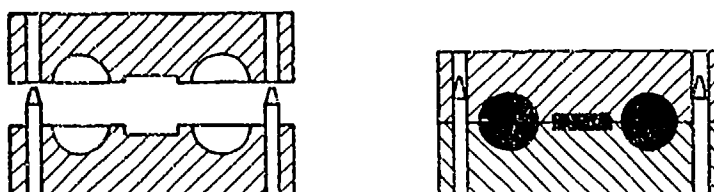


Fig. 3.7a - Compression molding

Compression molding is a slow process, since the entire rubber mass must reach temperature before the period of vulcanization begins. Sufficient time must be allowed to avoid uncured or undercured articles.

Injection molding (cf. Fig. 3.7b), as the name implies, involves injecting uncured, preheated rubber into a closed, heated mold under high pressure. Injection molding has several practical advantages over compression molding. It gives more uniform physical properties of the vulcanizate due to automatic cure cycling. The finished elastomer product also has better physical properties because the stock is held at higher temperatures for a shorter time. Injection molding generally gives better rubber-to-metal bonds than compression molding.

Injection molding is most useful when medium- or high-production quantities of an article are to be produced. It results in lower labor cost due to faster cure cycles and the elimination of having to prepare mold preforms as in compression molding. There is also a savings in raw materials.

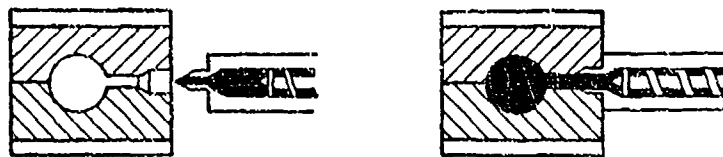


Fig. 3.7b - Injection molding

Transfer molding (Fig. 3.7c) is a variation of injection molding. It is useful in cases where the production volume does not justify the expense of fully automatic injection molding. In transfer molding, the injection feature is built into the mold, and a plunger forces the stock through a small opening into the mold cavity.



Fig. 3.7c - Transfer molding

Transfer molding is preferable to compression molding for the bonding of rubber to smaller delicate metal parts. The closed mold holds the parts in the proper position during the transfer and cure cycle so that there is no chance of parts being shifted or damaged.

Transfer molding is also better than compression molding for making detailed or intricate moldings. This is because the transfer mold maintains constant pressure on the elastomer stock so that it is evenly dispersed throughout the mold. In a compression mold, too much rubber may escape from the overflow grooves, causing incomplete filling of the mold cavity. On bonded parts, this loss of stock would cause a low degree of adhesion. Transfer molding also helps to eliminate any grain effects due to the method of filling the cavity, as sometimes occurs in compression molding, with a resultant uniformity of shrinkage in the finished product.

Rubbers are generally poor conductors of heat with coefficients of thermal expansion that are much higher than those of metals. This must be taken into account in designing molds for the vulcanization of rubber articles, since the finished unit will normally exhibit on the order of three- percent volume shrinkage when removed from the mold and cooled to room temperature. The type of compound; variations in rubber from batch to batch; and variations in cure time, temperature, and pressure will all affect the amount of shrinkage. For this reason, adequate dimensional tolerances in molds must be specified that will cover this inherent variability.

Since all rubber deforms, the close tolerances normally specified on metal parts are often unnecessary on rubber parts. The cost and effort of designing molds are also directly related to the tolerances required. In practice, transfer molding will permit a greater accuracy in precision molding than in compression molding. Tolerances on rubber-metal parts should be greater than on all-rubber parts. The tolerances should also be greater than on any individual metal component.

For rubber molded parts, a common starting point for agreement is a series of tables prepared by the Rubber Manufacturers Association (RMA). These are published in RMA's *Rubber Handbook*²⁶⁹. One source of this handbook is the Huntington Rubber Co. (Appendix B).

3.4 ADHESION

Attachment of elastomers to other types of polymers or various metals through the process of adhesion is of critical importance for many underwater acoustical applications. The ASTM has defined adhesion as the state in which two surfaces are held together by interfacial forces of attraction²⁷⁰. A complete treatment of adhesion could require a separate text in and of itself and is a topic outside the author's area of expertise. The works of Skeint²⁷¹ and Lee²⁷² are recommended for those who would like to pursue the topic in detail.

A good but somewhat brief survey treatment is given by Gent and Hamed²⁷⁰, who divide the science of adhesion into two broad categories²⁷⁰. These are the chemistry and physics of surfaces and interfaces and the mechanics of fracture of adhesive joints. Each of these is pertinent to the use of adhesives in underwater acoustical applications. Some of the factors involved in evaluating elastomer-to metal adhesion in sonar transducers have been discussed by Ting^{273,274}. References 275 through 277, available from Hughson Chemicals, review both the fundamental aspects of rubber-metal adhesion and factors involved in the selection of adhesives for bonding elastomers to various metals.

Adhesion between two different substances may involve either physical or chemical bonding²⁷⁸. Physical bonding involves either mechanical interlocking, physical adsorption between adhesive molecules and substrate molecules, or penetration of adhesive molecules into the substrate by diffusion. Mechanical interlocking is important in the bonding of porous materials such as textiles and paper, as well as some etched metals and plastics. Chemical bonding involves the formation of covalent or ionic bonds between molecules of the adhesive and substrate. It is this type of bonding that normally occurs between elastomers and adhesives.

It is possible to bond most elastomers by some means to practically all of the common metals. The choice of the elastomer to be used is an important consideration in the design of a bonded assembly with elastomeric materials. Natural rubber, SBR, chloroprene (neoprene), and NBR are used most often in bonded rubber parts. Butyl rubber, BR, CFM, ethylene-propylene (EPM), EPDM, polyurethane, and silicone rubbers are used to a smaller extent. Silicone rubbers, in particular are relatively difficult to bond to metals. Additionally, the choice of the cure system used for a particular elastomer may have a significant impact on its bondability.

A number of adhesives or adhesive systems are commercially available for bonding practically all types of elastomers. The Thixon series, manufactured by the Dayton Coatings and Chemicals Div. of the Whittaker Corp., is a wide product line for virtually all types of elastomers. The Chemlok series, manufactured by Hughson Chemicals, is another complete line

of adhesives for different types of rubbers. In addition, Products Research and Chemicals Corp. and Conap, Inc., make lines of primers and adhesives for their polyurethane compounds. Other companies, such as B.F. Goodrich, make general-purpose or specialty adhesives that may be suitable for a given application. A list of adhesive manufacturers is given in Appendix 4. Specific product information and manufacturers' recommended usages may be obtained from companies listed there.

Although the final selection of an adhesive should be based on the intended service application and the recommendations of the manufacturer, there are a number of general characteristics that an adhesive should possess in order to form a successful elastomer-to-metal bond²⁷⁵. The adhesive should readily wet the metal surface. It should be able to displace and absorb a reasonable amount of surface contamination from the metal or elastomer as well as any compounding ingredients that might migrate to the surface of the elastomer. Waxy materials, which may have been added to the rubber for antioxidation purposes, and plasticizers are particularly troublesome. The adhesive should be able to accommodate the wide variations in cure conditions used to vulcanize different elastomer compounds. It should have a sufficient amount of cohesion to resist sweeping in the uncured state. It should retain its desired properties in a variety of service situations and be able to maintain bond integrity throughout any chemical or mechanical post-bonding treatment. Most important, the adhesive should be compatible with the elastomer with respect to dynamic mechanical and physical static properties.

To obtain the desired bond strength for an elastomer-to-metal bond, it is essential that the substrates be properly prepared. Strict cleanliness of the surfaces to be bonded is important. The proper cleaning procedure will be determined by the substrate and type of contaminant. Refs. 275 through 277 and 279 give general guidelines for proper surface preparation, as well as specific recommendations for given metallic and non-metallic surfaces. Reference 275 also gives a process control checklist.

Two methods of surface preparation may be used: mechanical and chemical. Mechanical methods involve abrading surfaces with steel wool, a wire brush, or backed abrasives; blasting with sand, grit, or metal oxides; and machining or scoring the surface. Chemical or solvent cleaning may also sometimes have to be employed with mechanical methods. Chemical methods use inorganic reagents, such as mineral acids, or organic reagents to remove surface soils and contamination by chemical action, or react with metal surfaces to form metallic compounds.

The choice of the cleaning method will be influenced by several factors. Chemical treatments are generally less costly than mechanical methods. Mechanical cleaning offers greater versatility, however, since the same mechanical methods may be applicable to many different metals. Existing facilities may also help to determine whether mechanical or chemical processing is preferred. Environmental resistance requirements may also be important, since chemical methods often give enhanced resistance compared to mechanical cleaning.

Reference 279 gives a complete description of cleaning methods for a large number of metals, alloys, and plastics. It is suggested that the reader consult these for specifics. References 275 through 277 and 279 may be obtained upon request from the publisher. In addition, information on a number of commercially available cleaning and processing solutions, along with suppliers' names, may be obtained from the publishers.

Once an optimum surface has been obtained, it should be maintained until the primer or adhesive is applied. Exposure to dust, moisture, or other contaminants should be avoided. A useful and quick method to check for surface contamination is the water-break test. Distilled water should wet the surface of the substrate in an unbroken film. If this does not occur, either surface contamination has occurred or the surface preparation has been inadequate.

The bonding process may involve the bonding of either unvulcanized or vulcanized elastomers to metal. Bonding of metal to vulcanized elastomers is a much more difficult task. There are several reasons for this.

Vulcanization of the elastomer gives a crosslinked polymer that has often been compounded to optimize a certain characteristic, such as aging resistance or water-permeability resistance. These polymers are difficult to solvate, and it is difficult to obtain any degree of chemical crosslinking between the polymer and the adhesive. Contamination of the elastomer surface with metal-release agents, or with plasticizers or antioxidants that have migrated to the surface, makes wetting with the adhesive difficult and provides weak boundary layers.

A number of methods for solving these problems are discussed in Ref. 171. Basically, they involve cleaning the surface and then modifying it by either mechanical abrasion or buffing, cyclizing, isocyanate treatment, or chlorination. It is believed that the chemical treatments cause a reversion depolymerization, or oxidation of the elastomer surface²⁷⁵. With the possible exception of cyclizing, they slightly increase the surface roughness.

Cyclizing involves the use of various concentrated acids to modify the elastomer surface -- sulfuric acid being the most commonly used. Care should be taken not to over-treat the elastomer, as the surface will harden and become brittle.

Isocyanates have also been used as a pretreatment for bonding of vulcanized elastomers, particularly chlorinated ones. References describing the use of isocyanates may be found in Ref. 275.

A chlorine solution is sometimes used to treat vulcanized elastomers in order to improve adhesion to coatings. The following procedure is recommended²⁷⁵. A solution consisting of 100 parts by volume water, 3 parts by volume of 5.25% sodium hypochlorite solution (Clorox), and 0.5 parts by volume of 37% hydrochloric acid is prepared. Alternatively, chlorine gas may be bubbled through water. These solutions should be prepared and used in a well ventilated area.

The vulcanized elastomer is then immersed for 1 to 3 minutes, followed by a rinse in running hot or cold water. The elastomer is then dried in forced air. The immersion time may be varied to suit the particular elastomer. Rubbers with an 80 to 90 Shore A hardness may require more than 3-minutes immersion, while those in the 30 to 40 Shore A range can be treated in 1 minute or less²⁷⁵. It may also be necessary to increase the Clorox concentration to 6 volumes per 100 volumes of water for highly filled neoprene elastomers. The treatment time may also have to be extended to as much as 6 minutes.

A number of commercial systems are now available for bonding vulcanized elastomers to metals. Information on these may be obtained from the manufacturers. A list of adhesive manufacturers is given in Appendix 4.

The bonding of an unvulcanized elastomer to a metal takes place in several steps. After the metal surface has been prepared, a suitable primer is applied. A primer is usually necessary for maximum environmental resistance. The primer should be thoroughly dispersed and evenly applied. It should be applied in a thin coat and be completely dried before the first coat of adhesive is applied.

Several different methods may be used to apply the adhesive. Spraying, dipping, brushing, roll coating, tumbling, or any other suitable method may be used. The particular method of application chosen will depend on the size and shape of the metal parts, the number of pieces to be coated, and whether they are to be completely or partially coated. In any case, the adhesive should be thoroughly agitated prior to and during application. Each part should be coated with a uniform film of sufficient thickness to obtain the desired degree of adhesion. If more than one coat of adhesive is required, sufficient time between applications should be allowed to ensure that the solvent from the first coat has completely evaporated.

After application of the adhesive, the metal component is positioned in the mold. Unvulcanized rubber is then placed in the mold so that it contacts the adhesive surface. The normal curing cycle for the elastomer

is then initiated. During this time, the primer and adhesive cure by reaction, the elastomer is vulcanized, and a chemical bond is forced between the elastomer and the metal.

During vulcanization, adequate pressure should be applied to the mold. It is also important that the temperature be uniform throughout in multi-cavity molds. Nonuniformity will result in bond failure and overcure or undercure on some parts.

Care should be exercised in any post-bonding treatment. Use of liquid nitrogen in deflashing parts can cause bond failure if the joint is put under stress at a low temperature. Deflashing or cleaning by wire brushing, grinding, or machining may cause problems if excess heat is generated. Other procedures, particularly electroplating, may also cause failure. This may occur if the current density is too high, the adhesive is adversely affected by the plating bath, or the joint is highly stressed while it is being plated.

3.5 BOND FAILURES

Three basic procedures for testing adhesive joints are specified in ASTM D429. This standard provides a detailed set of symptom descriptions for bond failures. The ASTM specifications cover the majority of bond failures and are grouped into four basic designations: RC - failure at the elastomer-adhesive interface, CP - failure at the adhesive-primer interface, CM - failure at the metal-primer interface, and R - failure in the elastomer.

The last category can be further broken down to subcategories. Rubber failures may be classified as: SR - Spotty rubber, TR - Thin rubber, HR - Heavy rubber, or SB - Stock break. SR appears on the metal surface looking like splattered rubber. It is usually caused by contamination of the metal surface with dust or other foreign material prior to bonding. It may also be caused by ultrafast drying of the adhesive if it is applied by spraying. TR is an even but very thin residue of elastomer on the metal surface. It usually occurs with rubber stocks that are highly oil extended, as a

consequence of migration of oils to the rubber-adhesive interface. HR is a thick layer of rubber remaining on the metal surface and is indicative of an excellent bond. Failure occurs because the elastomer is stressed beyond its cohesive point. SB is a type of failure where it appears that the elastomer has folded back on itself and broken off.

Complete descriptions of other types of bond failures, possible causes, and suggested cures are contained in Ref. 275. This reference also contains photographic illustrations of the results encountered in different types of bond failures. A review of the applicability of the ASTM methods may be found in the article by Cutts²⁸⁰. A summary of a number of other methods for measuring adhesion may be found in the article by Bullett and Prosser²⁸¹. Additionally, a compilation of real-time data under varying exposure conditions for the durability of a number of high-strength adhesive types can be found in Ref. 282. It is suggested that the reader consult Refs. 275 through 277 and 279, along with the ASTM standards for further specifics of troubleshooting bond failures.

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CHAPTER 4

APPLICATIONS OF MATERIAL PARAMETERS TO DESIGN REQUIREMENTS

The discussion up to this point has hopefully given the reader some insight into the various factors that affect the physical and dynamic mechanical properties of elastomers, as well as how these are measured. The information presented on specific classes of elastomers in subsequent sections of this work is intended to give the reader a starting point in selecting a specific type of material for a particular use. The application of the basic concepts of polymer viscoelasticity to practical systems can be quite complex, since the desired acoustical functions vary widely from one application to another. For instance, compression set (ASTM D 395) and long-term creep behavior may be of critical importance in cases where elastomers are used as gaskets, mounts, or in a configuration where they will be clamped²⁸³. Conversely, these may be of relatively minor importance if the material is used as a sound-absorbing coating. Additionally, other factors such as permeability of the elastomer to water, gases, and chemical interactions with various fluids must be taken into account. Some of these are discussed in Appendix 5.

This section is primarily intended to be a brief discussion of how the viscoelastic properties of polymers are of importance for given design applications. As an example, the acoustical properties that an elastomer should possess in order to be a suitable transducer window²⁸⁴ are quite different from those it should possess in order to be used as a damping material. The former case, as is discussed in many texts on acoustics, requires that the elastomer possess a close acoustic impedance match to seawater at normal incidence over the desired temperature and frequency ranges of application, as well as low attenuation per wavelength to avoid internal losses. It should also possess a low insertion loss and a high echo reduction.

The theoretical equations treating the transmission and reflection of plane waves at normal incidence in multilayered media are treated in standard texts on acoustics such as Kinsler and Frey²⁸⁵. Such equations may be modified to incorporate effects due to acoustic dissipation in viscoelastic layers. The case of reflection and transmission of

viscoelastic dilatational and shear waves at both normal and oblique incidences has been treated by Cooper^{286,287} and Mott²⁸⁸. Various treatments²⁸⁹⁻²⁹³ have been used that incorporate complex longitudinal and shear phase velocities into existing theories for the interaction of sound with elastic plates. The transmission and reflection properties of a number of anechoic coatings have been studied as a function of angle of incidence, frequency, and pressure by Madigosky and Fiorito²⁹⁴. This was done by developing a model for the effective moduli and wave speeds for both dilatational and shear wave propagation, and using a transfer matrix technique for calculating acoustic propagation in a multilayered system of elastic/viscoelastic layers.

Other areas in which the dynamic mechanical properties of polymers play an important role are in vibration isolation and vibration control. Wetton²⁹⁵ has discussed the mechanical characteristics for vibration damping materials in terms of the frequency and temperature dependence of the viscoelastic properties of polymeric materials. Snowdon^{296,297} and others^{298,299} have treated the role of internal damping of rubber-like materials in vibration isolation. Use of polymeric materials in free-layer and constrained-layer damping configurations has been discussed in the literature by Ungar and Kerwin³⁰⁰⁻³⁰⁴ and others^{305,306}. In this section, we briefly review the viscoelastic requirements for three different types of vibration-control applications. These are the simple mount system, free-layer damping, and constrained-layer damping.

4.1 VIBRATION ISOLATION SYSTEMS

Vibration isolation is often desirable in circumstances where a rigid body is vibrating steadily under a periodic force, so that it is necessary to prevent the transmission of this force onto its surroundings. This is often accomplished with the insertion of an elastomeric isolator. An idealized representation of a one dimensional model of this situation is shown in Fig. 4.1. An element of mass M is supported by a linear rubber-like material placed on a foundation. A sinusoidally varying force F_1 is applied to or generated within the mass M . The force F_2 is transmitted to the foundation. The equation of motion for such systems is well

known^{307,308}. The fraction of the force transmitted to the foundation is known as the transmissibility, T . It can be shown that the T of such a system is given by

$$T = \frac{\sqrt{(1+\tan^2 \delta)}}{\sqrt{[1-(\omega/\omega_0)^2 (E_0/E')]^2 + (\tan^2 \delta)}} , \quad (24)$$

where $\tan \delta$ and E' are the viscoelastic parameters (loss tangent and storage Young's modulus) for the rubbery material. The quantity E_0 is the value of E' at the resonance frequency of the system. This is defined as the frequency at which T becomes infinitely large in the absence of any damping. The quantity ω_0^2 may be expressed as

$$\omega_0^2 = k \cdot E_0 / M , \quad (25)$$

where the constant k has the dimensions of length. The value of k will depend upon the shape of the rubber element.

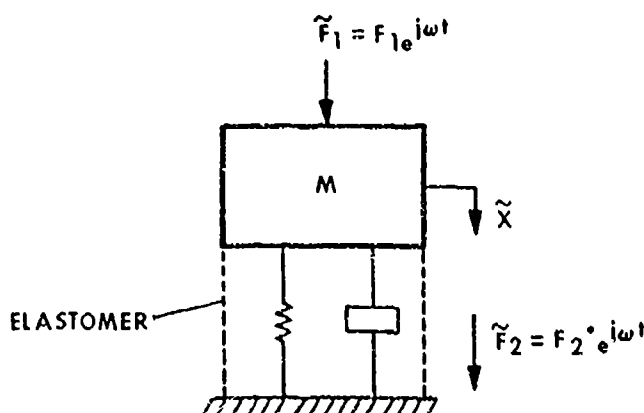


Fig. 4.1 - Simple mount system

The spring and dashpot combination in Fig. 4.1 is a mechanical convenience for purposes of modeling, rather than an exact representation of the properties of the system. Also, it does not account for wave effects that may occur at higher frequencies. A more complete discussion of this may be found in Refs. 296 and 297. These effects are neglected for the purpose of the present discussion, since they will not seriously affect the performance of rubbers with high internal damping at low frequencies^{296,297}.

For purpose of illustration, the simple mount equation has been used to calculate the transmissibility of several chlorobutyl elastomers developed in this laboratory³⁰⁹. This was done by using the specific frequency and temperature dependencies of their viscoelastic properties, as determined from experimentally determined master frequency curves.

Figure 4.2 illustrates the transmissibility curves obtained at 263.15K for four red lead-cured chlorobutyl elastomers (cf. Ch. 5, Tables 5.3 and 5.6) with different types of carbon black. An arbitrary resonance frequency of 100 Hz has been assumed. Transmissibility is plotted on a dB scale. Positive values of the transmissibility indicate that undesired magnification of vibration has occurred, while negative values indicate that the input force has been attenuated by the rubber material. It can be seen that the elastomer with no carbon black filler gives greater vibration isolation at resonance, but its performance falls off quickly at higher frequencies. Likewise, the three different types of carbon black fillers give very similar transmissibility curves just as their viscoelastic properties closely resemble each other (cf. Figs. 4.3 and 4.4). Again, the more lossy SAF black-filled elastomer gives greater isolation at resonance but does not perform as well at higher frequencies.

Figure 4.5 shows the calculated transmissibility curves for resin-cured chlorobutyl at various loadings of an HAF (N347) black at 293.15K and 100 Hz. Again, the higher damping rubber with no black suppresses vibration better at resonance, but its performance is inferior at higher frequencies. Increasing the loading of black increases the transmissibility at resonance but gives better vibration isolation at higher frequencies. Changing the temperature of this system would involve shifts in the resonant frequency and minor adjustments in the M/k ratios, due to changes in the storage modulus of the elastomer and shifts in the peak of the loss tangent to different frequencies (cf. Figs. 1.4 and 1.5).

A consideration of Figs. 4.2 through 4.5 allows us to draw the following conclusions: (1) Only vibrations beyond the system resonance may be effectively isolated. (2) Very lossy elastomers more effectively suppress vibration at resonance but do not work well at higher frequencies.

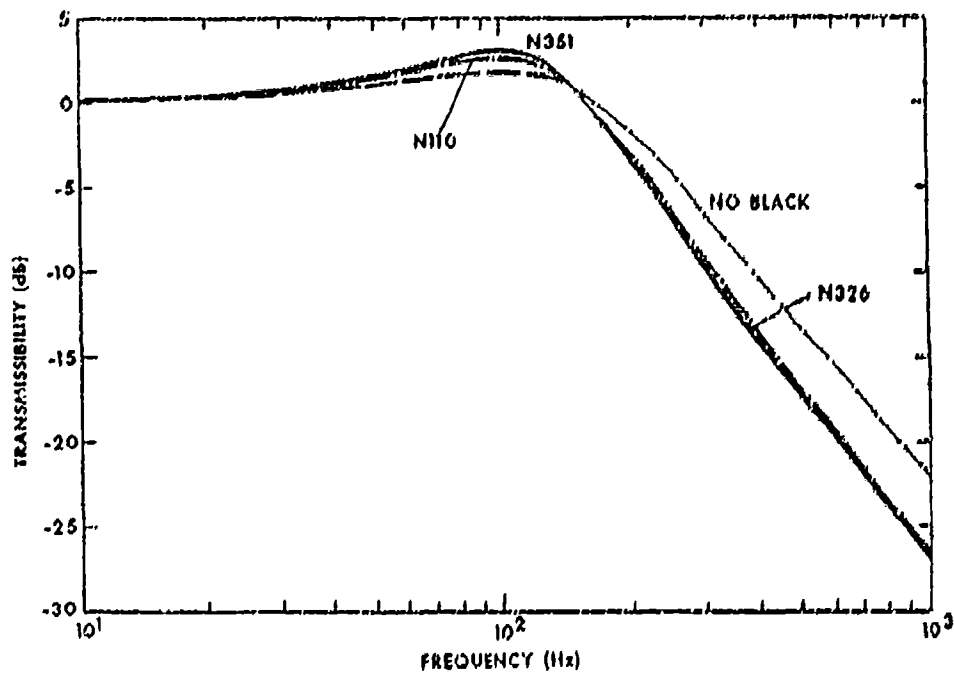


Fig. 4.2 - Plot of calculated transmissibility vs frequency at 293.15K for red lead-cured chlorobutyl reinforced with no black and 85 phr of three types of black

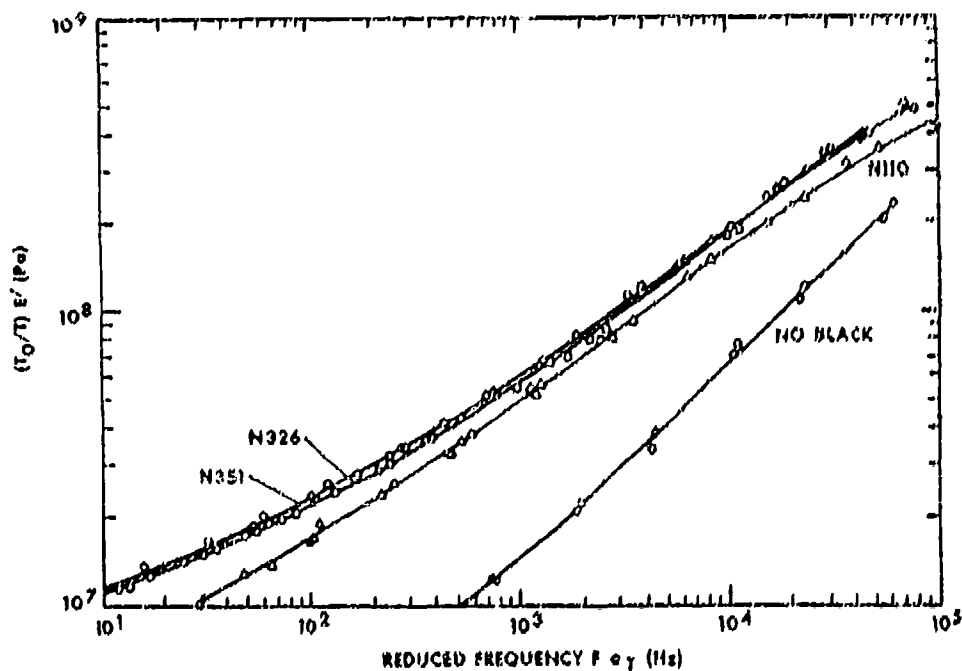


Fig. 4.3 - Plot of storage Young's modulus vs reduced frequency at 293.15K for red lead-cured chlorobutyl reinforced with no black and 85 phr of three types of black

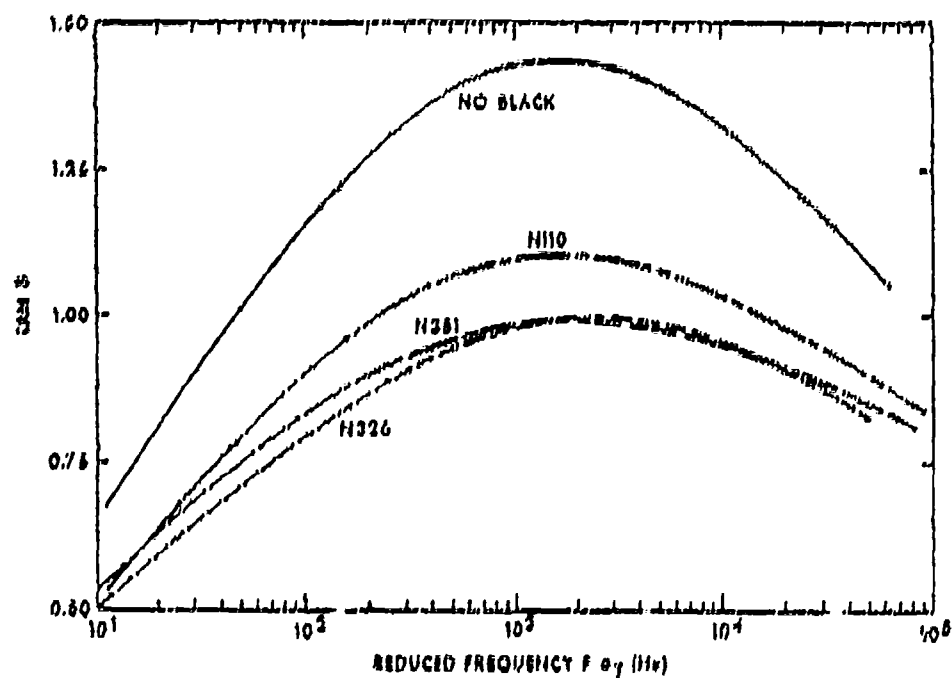


Fig. 4.4 - Plot of loss tangent vs reduced frequency at 288.15K for red lead-cured chlorobutyl reinforced with no black and 45 phr of three types of black

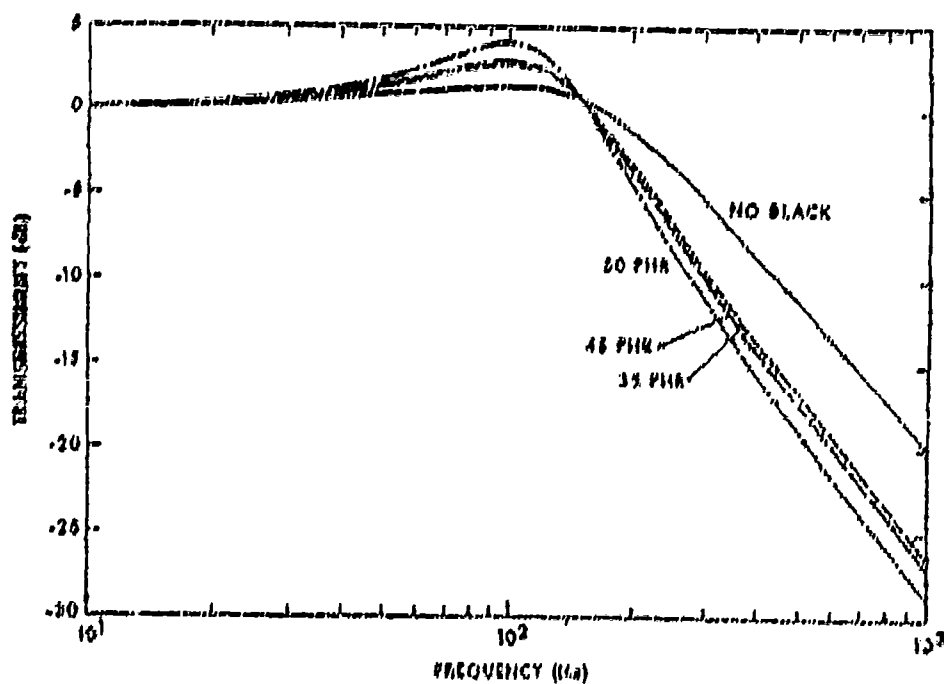


Fig. 4.5 - Plot of calculated transmissibility vs frequency at 288.15K for resin-cured chlorobutyl reinforced with no black and three loadings of N64V black

Thus, use of carbon black fillers will increase the rate of attenuation at higher frequencies. (3) Elastomers whose rate of change of E' with frequency or temperature is minimal will be more effective at attenuating vibrations beyond resonance.

One other point is worth noting here. The calculated transmissibility curves are based on viscoelastic properties measured at small strain amplitudes. Since the properties of carbon black-filled rubbers are strain dependent, it might be thought that their performance in anti-vibration mounts might differ from that predicted here. However, as Snowden^{296,297} has pointed out, well-designed mounting systems will normally possess natural resonant frequencies that fall significantly below the spectrum of frequencies that the system is designed to isolate. Secondly, even if the elastomers exhibit nonlinear behavior above resonance, the dynamic stiffness of the rubber would decrease in magnitude⁶⁹ and the loss tangent would increase, causing a decrease in the transmissibility of the system and increasing the effectiveness of the mounting system.

4.2 STRUCTURAL DAMPING

Another very important area of application of polymeric materials is in structural damping. Structural damping may be considered to arise in cases where the vibrating component is structurally flexible, such as a plate or bar, so that it will be subject to flexural or extensional waves under dynamic loading. Attachment of a damping layer will serve to attenuate the amplitude of a steady-state bending wave or increase the decay rate of a transient wave by increasing the dissipation factor of the composite panel. Two typical applications are illustrated in Figs. 4.6 (a) and (b). These are free-layer and constrained-layer damping. We consider the case of free-layer damping first.



Fig. 4.6 - Use of a viscoelastic layer in damping:
 (a) extensional type
 (b) simple three-layer constrained shear type

Free-layer damping is considered to arise primarily from extensional deformation of a viscoelastic layer attached to a plate vibrating in flexure. As shown in Fig. 4.6 (a), the viscoelastic layer will be deformed through an angle θ . The structural loss factor of the composite will be proportional to the loss tangent of the viscoelastic layer, the relative thicknesses of the two layers, and the ratio of the storage Young's modulus of the damping layer and the base plate. More specifically, the relationship given by Oberst³⁰⁸ is

$$\eta = \frac{\tan \delta \cdot eh(3 + 6h + 4h^2)}{1 + eh(3 + 6h + 4h^2)}, \quad (26)$$

where η is the structural loss factor of the composite, $\tan \delta$ is the loss factor of the viscoelastic layer, e is the ratio of the Young's modulus of rubber to metal, and h is the ratio of the thickness of the damping layer to the base plate (H_1/H_2).

Examination of Eq. (26) shows that attainment of a high structural-loss factor for free-layer damping requires both a high loss tangent for the viscoelastic layer and a storage modulus comparable to that of the backing plate. These two requirements are difficult to meet simultaneously, since the loss tangent will reach its maximum in the glass transition region, while the storage modulus has not yet reached a high value. Furthermore, since the two quantities are related²² by the approximate relationship

$$\tan \delta \approx \frac{2}{\pi} \cdot \frac{d(\ln E')}{d(\ln \omega)} \quad (27)$$

for most polymeric materials, use of techniques such as the addition of reinforcing fillers cannot be used to adjust one quantity independently of the other. Careful selection of carbon black will allow an increase in E' , while causing only a slight decrease in $\tan \delta$ for most elastomers in the glass-rubber transition zone. Also, the properties of these materials are quite sensitive to temperature (cf. Figs. 1.4 and 1.5) so that optimum damping will be obtained only over a relatively narrow range of temperatures for a given frequency range.

For purposes of illustration, we have used the viscoelastic properties of the chlorobutyl elastomers discussed in the previous section to calculate the structural-loss factors expected for a 0.5-in. thickness of elastomer on a 0- to 0.375-in. brass backing at different temperatures. Figure 4.7 shows the calculated structural-loss factor at 263.15K for several of the red lead-cured chlorobutyls filled with different types of black. A comparison of Fig. 4.7 with Figs. 4.2 and 4.3 shows that, although the use of black has caused a decrease in the loss tangent of the damping layer, the concomitant increase in the storage modulus has been enough to offset this and cause an increase in the damping of the composite. Figure 4.8 illustrates that for a given thickness of elastomer and backing plate, the structural-loss factor will decrease significantly for a stiffer backing material.

An examination of Fig. 4.9 shows that additional loading of a given type of black within a formulation will increase free-layer damping. However, varying the temperature over a 30°C range will have a considerable effect on the damping of the composite (cf. Fig. 4.10), due to the temperature dependence of the damping layer itself.

4.3 CONSTRAINED-LAYER DAMPING

The situation encountered in constrained-layer damping is somewhat more complex. An example of a three-component constrained layer is shown in Fig. 4.6 (b). This consists of a viscoelastic layer coated onto a rigid

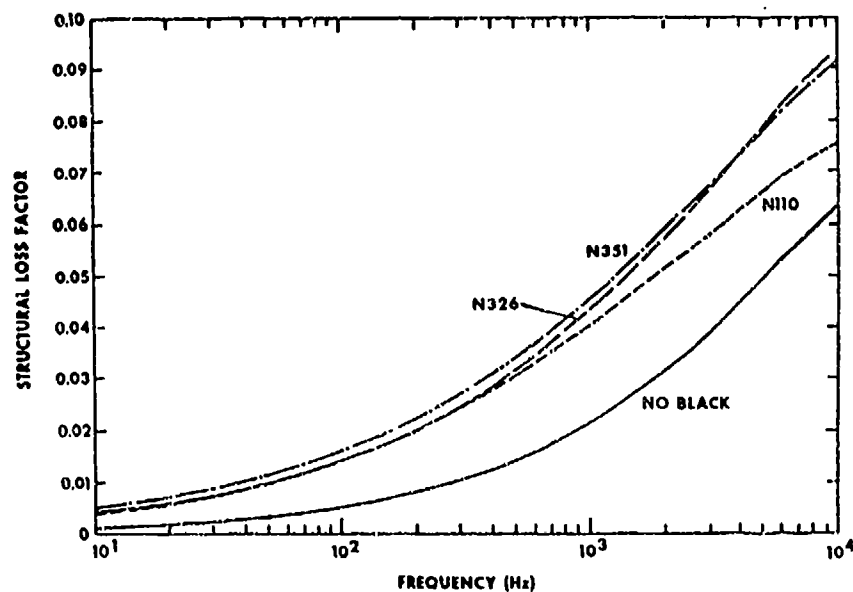


Fig. 4.7 - Calculated structural loss factor vs frequency at 288.15K for extensional damping of 2.05-cm brass coated with 1.2-cm red lead-cured chlorobutyl reinforced with no black and three different types of black

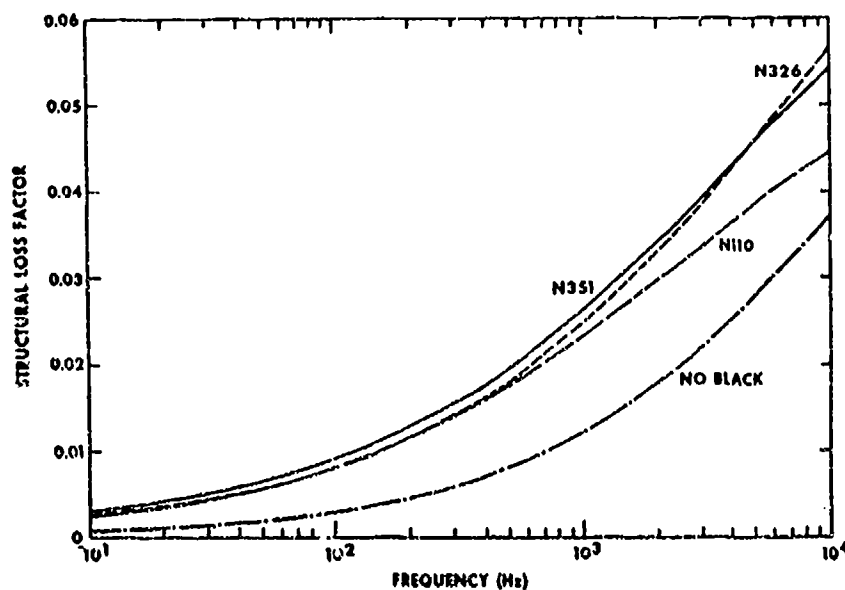


Fig. 4.8 - Calculated structural loss factor vs frequency at 288.15K for same formulations as in Fig. 4.7 on a 2.05-cm steel backing

substrate but constrained by a stiff top plate. Here, the material is deformed through an angle ϕ , which is greater than θ . The structural-loss factor will depend upon the shear storage modulus of the viscoelastic layer and its loss tangent, as well as the relative thicknesses of the various layers. The optimum thickness ratios of the layers can be computed for different ranges of the loss factor of the viscoelastic material. The choice of the thicknesses of the damping layer, the base plate and the constraining layer will affect the point at which the structural loss factor will take on its maximum value with respect to temperature or frequency. For most cases, optimization of the damping requires that the shear storage modulus of the viscoelastic material vary linearly with frequency and that its loss tangent be fairly high.

A complete treatment of the theory of constrained-layer damping and its application to the solution of various vibration-control problems can be found in Refs. 297 through 303. In the present case, we have used the treatment of Kerwin³⁰³ to predict the performance to be expected from the chlorobutyls used in a simple constrained-layer configuration. A 1-in.-thick substrate of brass was considered to be coated with a 0.04-in.-thick layer of rubber and constrained with a 0.08-in.-thick top plate. The density of the brass was 7.47 g/cc and its Young's modulus was 110 GPa. The shear modulus of the rubber layer was calculated from the measured Young's modulus by assuming a Poisson's ratio of 0.5. The effects of any type of structural adhesive were not considered.

For purpose of illustration, we consider the behavior of a resin-cured chlorobutyl at different loadings of the same (HAF) black and a single loading of black at different temperatures. Figure 4.11 illustrates the effect of increasing carbon loading at low temperature. It can be seen that the rubber with no black actually offers better damping performance at low temperatures. Increasing the temperature by 20°C changes the situation considerably, as is shown in Fig. 4.12. This may be attributed to the lower temperature sensitivity of the shear modulus of the more highly filled rubbers and the fact that the peak in the loss tangent curve will tend to broaden and shift to higher frequencies at any given temperature as the loading of black is increased.

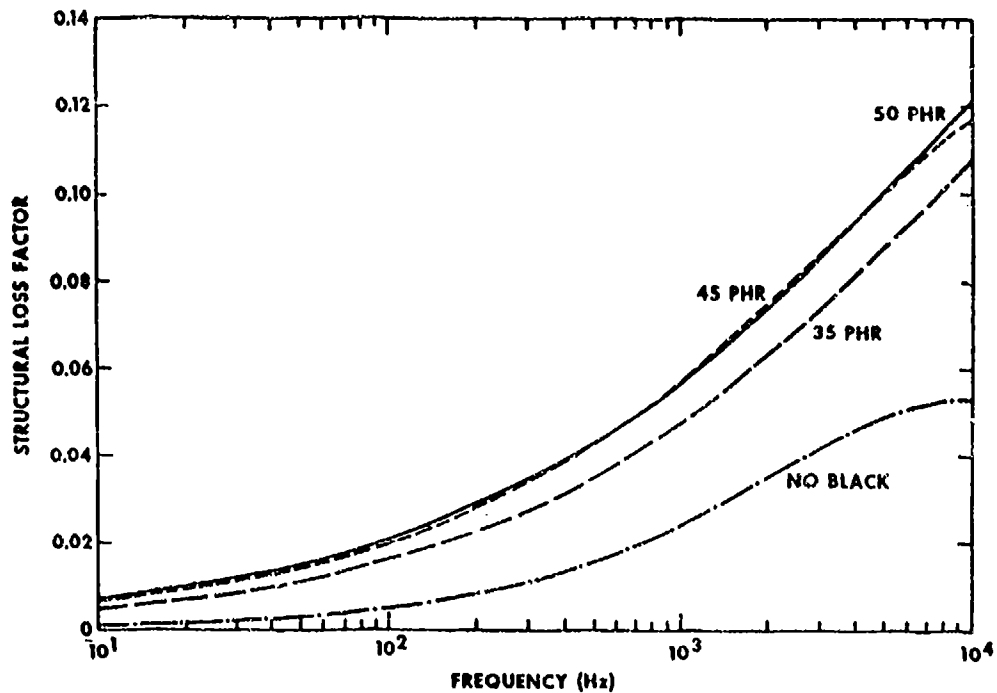


Fig. 4.9 - Calculated structural loss factor vs frequency at 263.15K for extensional damping of 0.95-cm brass coated with 1.2-cm resin-cured chlorobutyl at various loadings of N347 black

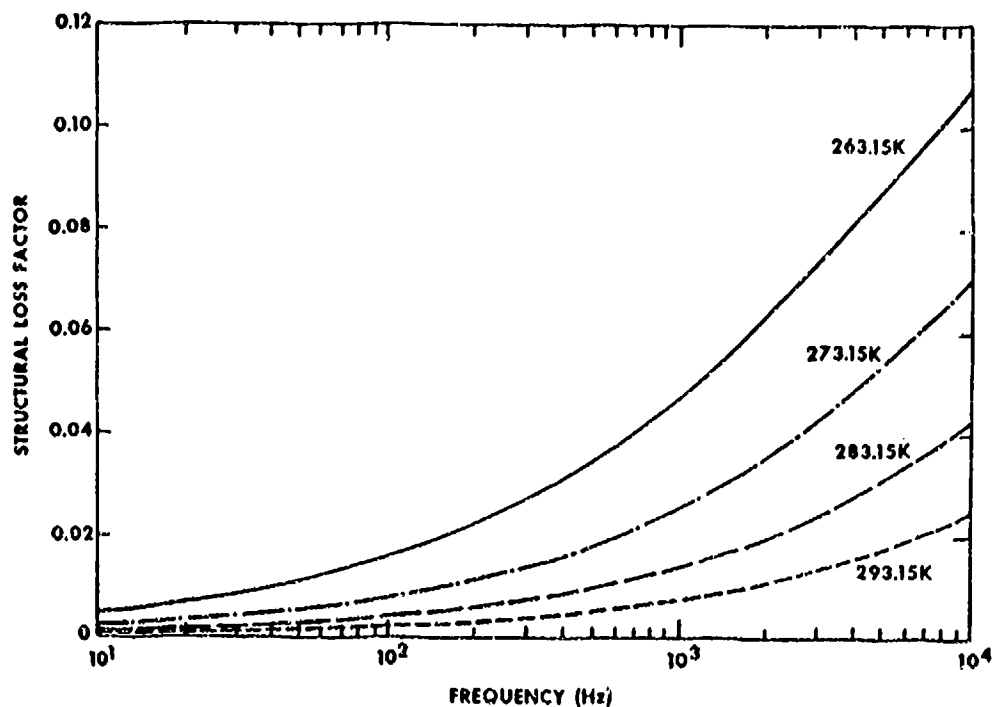


Fig. 4.10 - Effect of temperature on extensional damping on 1.2-cm resin-cured chlorobutyl reinforced with 35 phr N347 black on 0.95-cm brass backing

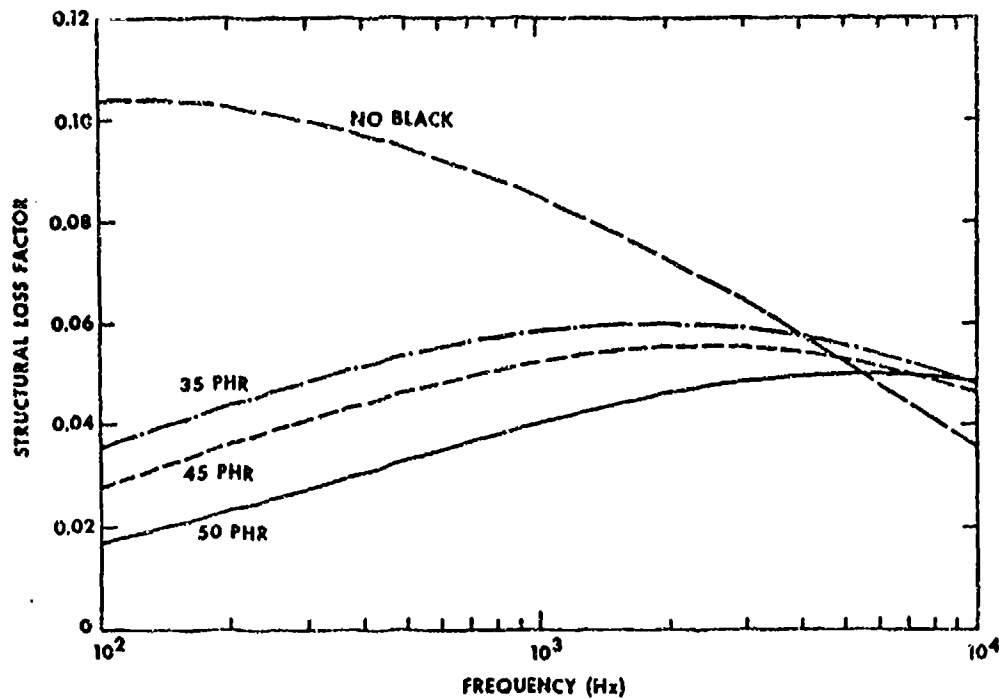


Fig. 4.11 - Calculated structural loss factor vs frequency for constrained-layer configuration at 288.15K using 2.5-cm base plate, 0.25-cm cover, and 0.15-cm resin-cured chlorobutyl at various loadings of N847 black

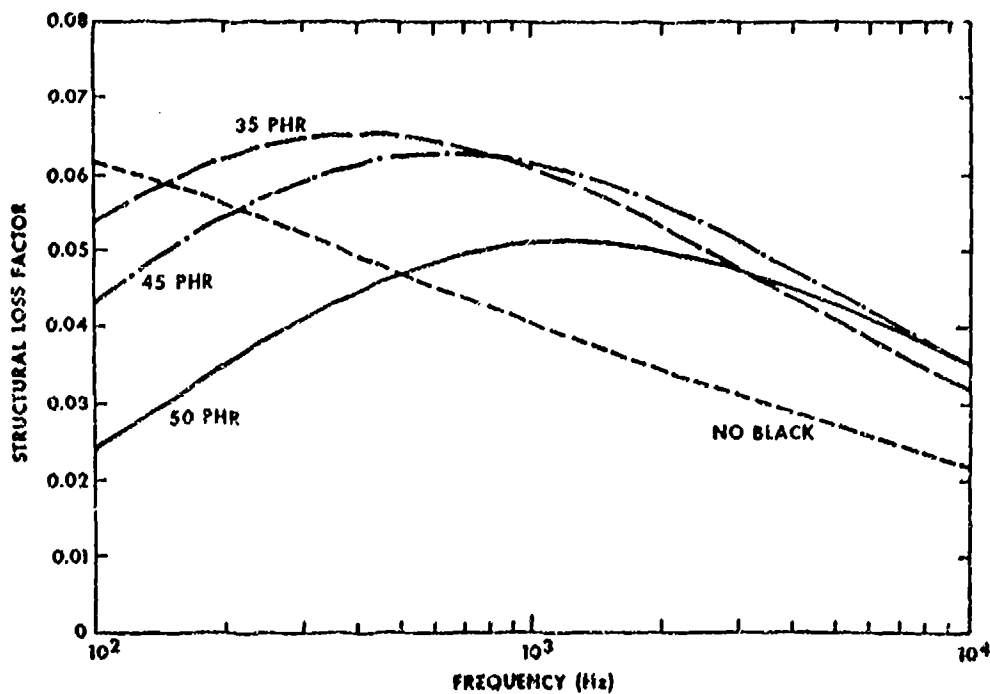


Fig. 4.12 - Calculated structural loss factor vs frequency for same formulations and conditions as in Fig. 4.11 at 388.15K

Figure 4.13 shows the predicted behavior of a resin-cured chlorobutyl loaded with 35 phr of an HAF black in a constrained-layer configuration as a function of temperature. Comparison of Figs. 4.10 and 4.13 shows that the damping performance of a constrained layer is much more dependent on the temperature and frequency behaviors of the viscoelastic layer, with maximum damping being obtained at intermediate frequencies and temperatures for the configuration considered here. The range of percentage critical damping is from 1 to 3% over the temperatures and frequencies considered. Use of other thickness ratios or multiple layers would give different structural-loss factors.

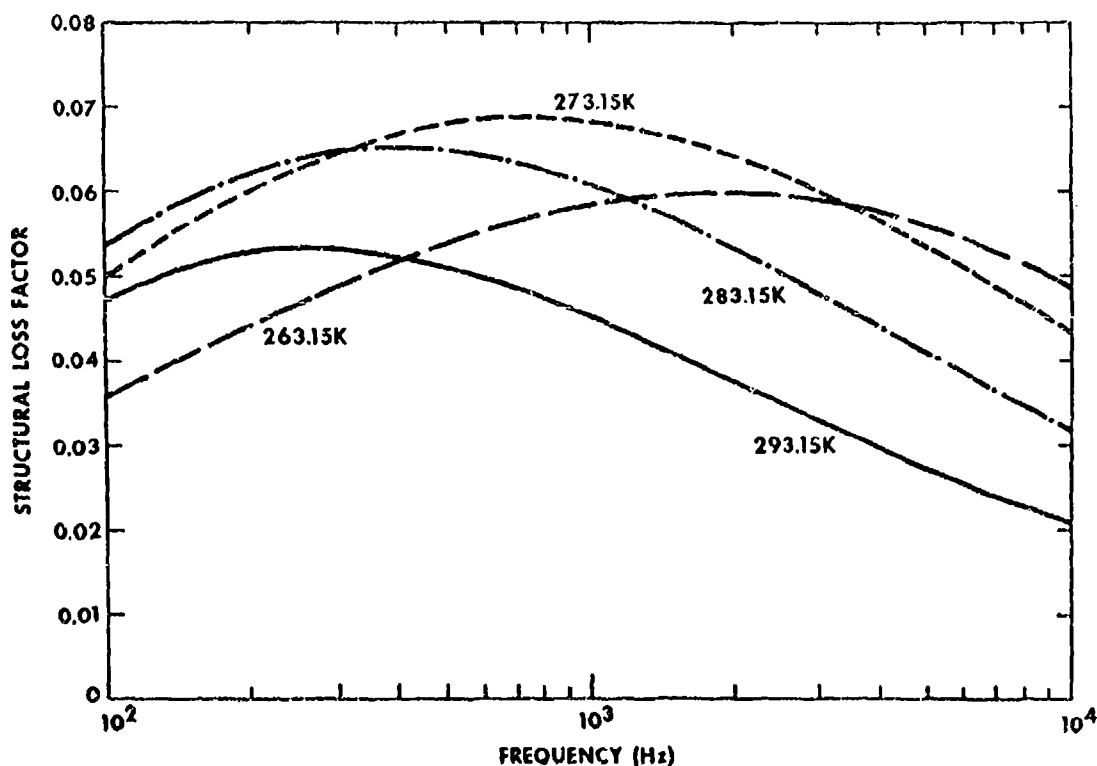


Fig. 4.13 - Calculated structural loss factor vs frequency as a function of temperature for resin-cured chlorobutyl reinforced with 35 phr N347 with same constrained-layer configuration as Figs. 4.11 and 4.12

Although the results of calculations such as those presented here may not be in exact agreement with experimentally measured configurations, they are useful in predicting trends and should be helpful in preliminary design choices. An experimental determination of the temperature and frequency dependence of polymeric materials, coupled with the type of modeling

described here, provides a convenient method of assessing the relative merits of various types of polymeric materials in the design of vibration-control systems.

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CHAPTER 5

BUTYL (IIR) AND CHLOROBUTYL (CIIR) RUBBERS

5.1 GENERAL INFORMATION

Butyl and chlorobutyl rubbers are given the ASTM D 1418 designations of IIR and CIIR, respectively. The two materials are very similar chemically and will be discussed here as one class of elastomer. Butyl rubber is produced by copolymerizing isobutylene with small amounts of isoprene (1.5 to 4.5%). The preparation of butyl rubber is normally carried out at -140°F using an aluminum chloride catalyst³¹⁰. The material is prepared directly as a crumb stock without going through a latex stage. Butyl rubber possesses a lower level of unsaturation than natural rubber so that cure systems must be highly reactive to initiate crosslinking. However, unsaturation due to the isoprene present is sufficient to allow the use of classical sulfur vulcanization.

The lower degree of unsaturation gives butyl rubber very good oxidation and ozone resistance. The proportion of isoprene can be varied from low for good ozone, chemical, and flex resistance to higher values for improved tensile and abrasion characteristics. Like NR, IIR reinforces itself by crystallizing when it is stretched. Use of reinforcing fillers does not offer a significant improvement in tensile strength, although it does increase tensile modulus and resistance to tearing³¹⁰. Commonly used fillers and reinforcing agents include both carbon black and mineral fillers. Carbon blacks provide superior reinforcement compared to mineral fillers, with smaller particle sizes providing higher tensile strengths and Shore hardness. Dispersion of the black is very important to avoid a reduction in tensile strength.

Butyl rubber has outstanding permeation resistance to both gases and water. It possesses excellent resistance to most acids and bases and to a wide variety of inorganic salts. Upon exposure to organic solvents, butyl reacts in the typical manner of a hydrocarbon rubber. It exhibits swelling in the presence of hydrocarbon solvents, such as hexane, kerosene, gasoline, Shell-Sol, or Isopar. It is relatively unaffected by polar

solvents such as alcohols, ketones, esters, and glycols. Butyl rubber is also resistant to animal and vegetable oils. It is particularly suited for use with linseed, cottonseed, and castor oil. However, it is attacked by chlorinated solvents such as chloroform or carbon tetrachloride. It is also susceptible to attack by halogen gases³¹¹.

Butyl rubber has excellent dielectric properties and electrical insulation resistance due to the fact that it is a non-polar hydrocarbon rubber. Additionally, its resistance to heat, ozone, and weathering make it attractive for electrical applications. Other notable characteristics of this material include its good abrasion resistance and high internal damping. This latter quality makes butyl particularly attractive for shock and vibration applications.

Chlorobutyl rubber is prepared by the controlled halogenation of butyl rubber gum stock (normally by passing gaseous chlorine through a solution of butyl in hexane). The two commonly available commercial grades, Exxon HT1066 and HT1068, both contain 1.1 to 1.3% by weight of chlorine. This normally corresponds to slightly more than 1-chlorine atom per isoprene unit. Since the introduction of the chlorine takes place by a substitution, the unsaturation of the polymer backbone is not changed. Chlorobutyl is more reactive to cure systems than is butyl, due to its dual chemical functionality (vulcanization may occur due to reaction at the chlorine or by reaction at sites of unsaturation in the polymer backbone).

Chlorobutyl retains the favorable properties of butyl, including its excellent ozone and weather resistance, its low permeability to gases and water; its excellent chemical resistance, its high damping, and its good intrinsic electrical properties. In addition, due to its greater reactivity with cure systems, chlorobutyl possesses a faster cure rate, the ability to cure with co-blends of other types of elastomers, superior heat resistance due to stable crosslinks formed by relatively simple cure systems, and good compression set resistance and retention of dynamic properties under severe service conditions.

5.2 CURE SYSTEMS

Butyl rubbers can be crosslinked by essentially the same activating and curing systems used for natural rubber (Ch. 8). Processing aids, such as petroleum oils or paraffin, are necessary to allow rapid mixing of formulations. The use of antioxidants should be considered for the faster curing grades with a high degree of unsaturation. As with other types of general-purpose elastomers, sulfur can be used as the basic crosslinking agent. Due to the low degree of unsaturation, ultra-fast accelerators, such as thiurams or dithiocarbamates, must be used to obtain commercially acceptable cure rates. Secondary accelerators, such as thiazoles or guanidines, may be added to modify elastomer properties. Zinc oxide and a fatty acid are also used. The mechanism of the sulfur cure is discussed in Ref. 312. Sulfur cures may pose a problem for transducer applications if the rubber material is in the vicinity of silver electrodes or solder joints. In any type of sulfur cure, a certain amount of free sulfur will be present in the vulcanized rubber. This may cause corrosion of solder joints or electrodes.

Dinitrosobenzene was the first sulfurless curing agent that was used for butyl polymers^{312,313}. P-dinitrosobenzene, the most common isomer, was found to be an extremely active crosslinking agent at low concentrations and room temperature. Its practical use was limited to partial crosslinking to strengthen the polymer and to reduce flow or deformation in compounded stocks prior to complete curing³¹². The quinone dioxime cure³¹⁴ is a more practical version of this cure. Oxidizing agents, such as lead oxide and benzothiazyl disulfide or halogen donors such as chlorotoluene sulfenamide^{312,315}, are used *in situ* to oxidize the quinone dioxime to dinitrosobenzene. Sulfur donors, such as MBTS, are normally used with these cures.

Methylol phenol resins offer another alternative to sulfur cure systems. Catalyzing agents such as stannous chloride or zinc oxide are normally used with this curing agent. Substitution of the hydroxyl substituent of the methylol group with bromine results in a resin that is self-curing. It provides good scorch safety, as well as a high degree of

heat and ozone resistance, good flex resistance, and low compression set. This material (commercially marketed as Schenectady SP1066 resin) has been found to give results with other types of elastomers, including chlorobutyl.

A number of accelerator types may be used for both butyls and chlorobutyls. These are summarized in Tables 4 and 5 of *The Vanderbilt Rubber Handbook*³¹⁰.

The Young's storage modulus and loss tangent are shown in Figs. 5.1 and 5.2 for a butyl elastomer that is used in standard hydrophones at USRD. This material is based on variations of the quinone dioxime cure system. The formulation is given in Table 5.1. This material also has suitable electrical properties to allow it to be used as a primary insulator.

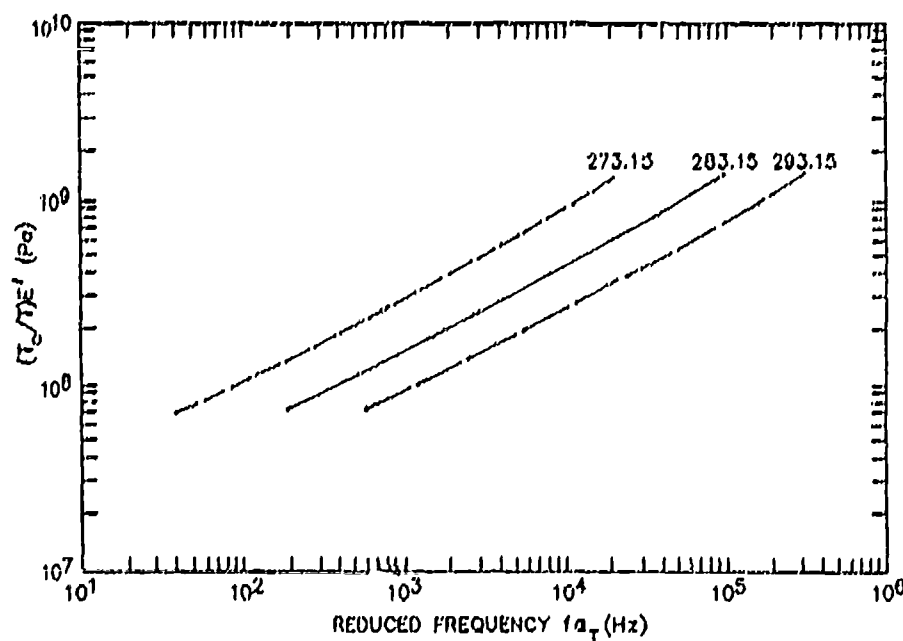


Fig. 5.1 - Plot of storage Young's modulus vs reduced frequency for Butyl 74821 at three temperatures

Due to the dual chemical functionality of chlorobutyl, a variety of cure systems can be used. Ultrafast cure accelerators are not as critical as for butyls. Sulfur may be used for the curing of chlorobutyl by

reaction of the unsaturation, or with zinc oxide or zinc chloride resulting in a complex ionic cure mechanism^{312,316,317}. Amine systems³¹⁶ may also be used to cure chlorobutyl, typically with magnesium oxide as an acid acceptor. Brominated phenolic resins are also useful cure systems for chlorobutyl. Another curative that has been evaluated for chlorobutyl is 3-methyl-thiazolidine-thione-2³¹⁸. It typically gives improved physical properties compared to sulfur cures.

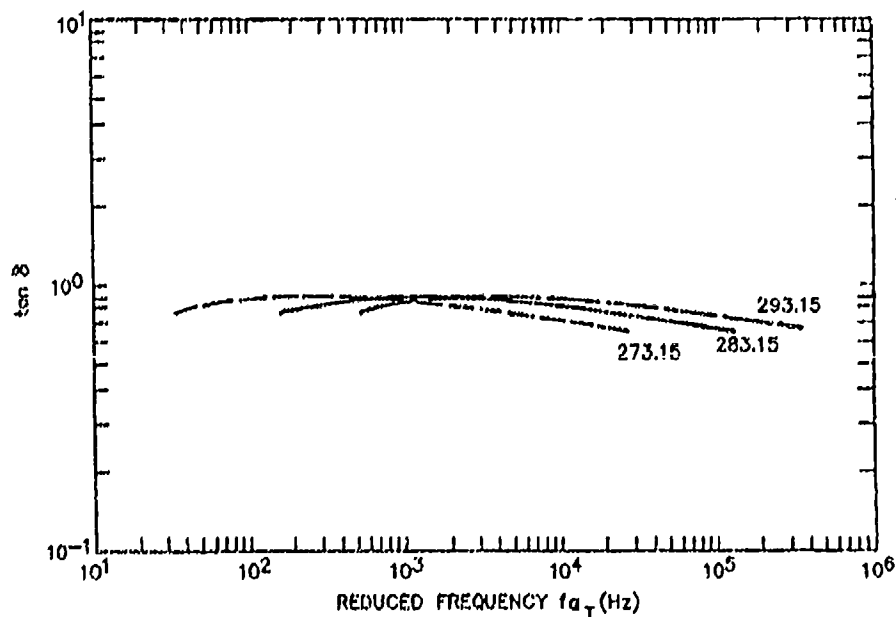


Fig. 5.2 - Plot of loss tangent vs reduced frequency for Butyl 70821 at three temperatures

Some of the more important cure systems, their properties, and areas of potential application are given in Ref. 316. These are appropriate starting places for developing chlorobutyl formulations, with modifications as necessary for specific applications. Filler type and loading, processing and cure conditions, and end-use requirements will all help to determine the particular cure system most suitable for a particular situation.

TABLE 5.1 - BUTYL 70821

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
Enjay Butyl 217	100.0
Calcined Clay	85.0
Whiting	40.0
EPC Black	10.0
Red Lead	9.0
Dibenzo GMF	6.0
Polyethylene	6.0
Zinc Oxide	5.0
Duraffin Wax	4.0
Sulfur	0.8
Stearic Acid	0.5
Polyac	0.15

Total parts by weight = 266.45

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1476.0	kg/m ³
Cure Temperature	153	°C
90% Cure Time	60	min.
Tensile Strength	4.8	MPa
Ultimate Elongation	500	%
300 % Modulus	3.1	MPa
Vol. Resistivity	4.3x10 ¹⁴	ohm.cm
Dielectric constant	3.59	

$$\log a_T = -4.78(T - 283.15)/(81.1 + T - 283.15)$$

$$\log (E' \text{ or } \tan \delta) = \sum a_n [\log \text{freq (Hz)}]^n$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	6.4995392	-0.982051734
a_1	0.872534178	0.731116682
a_2	-0.175356776	-0.179933748
a_3	0.0287032331	0.0132569466
a_4	-0.0014491222	0

Variations of some of the cure systems given in Table 3 of Ref. 316 have been evaluated in this laboratory³⁰⁹. Four different types of cure systems were chosen. These are summarized in Table 5.2. In each case, samples with no black and 50-phr loadings of a GPF (N660) and a medium thermal (N990) black were used. The first of these, the red lead-ethylene thiourea cure system, is currently used at USRD as chlorobutyl formulation H862A. Its composition and typical physical properties are summarized in Table 5.3.

TABLE 5.2 - FORMULATIONS FOR CHLOROBUTYL CURE SYSTEMS

COMPONENT	PHR			
	1	2	3	4
HT-1066	100	100	100	100
Red Lead	10			
Stearic Acid	1	1	1	1
AC Polyethylene 617	3			
DPG	2		2.5	
MgO	1	0.5		
ZnO	5	5		5
ETU	1.5		1.5	
TMTM		1		
MBTS		2		2
Poly DNB		0.25	0.25	0.25
Litharge		10		
SP-1055 (Schenectady)				4

TABLE 5.3 - FORMULATION AND PHYSICAL PROPERTIES FOR CHLOROBUTYL H862A

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
Chlorobutyl HT1066	100.0
Sterling V Black	50.0
Red Lead	10.0
Zinc Oxide	5.0
AC Polyethylene 617	3.0
Diphenylguanidine	2.0
NA-22	1.5
Maglite M	1.0
Stearic Acid	<u>1.0</u>

Total parts by weight = 173.5

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	59	
Tensile Strength	9.84	MPa
Ultimate Elongation	310	%
300% Modulus	9.66	MPa
Density	1180.6	kg/m ³
Volume Resistivity	1.29×10^5	ohm·cm
Cure Temperature	155	°C
90% Cure Time	94	min.

$$\log a_T = 4588 (1/T - 1/T_0)$$

$$\log (E' \text{ or } \tan \delta) = \sum a_n [\log \text{freq (Hz)}]^n$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	6.8999	-0.62606
a_1	0.18410	0.46148
a_2	0.021884	-0.10894
a_3	0.014459	0.0075705
a_4	-0.0022212	

The longitudinal wave speed at low frequencies has been determined by Lastinger and Groves³¹⁹ as a function of temperature and hydrostatic pressure for this material. This is shown in Fig. 5.3. Representative frequency and temperature behaviors of its Young's modulus and loss tangent are shown in Figs. 5.4 and 5.5

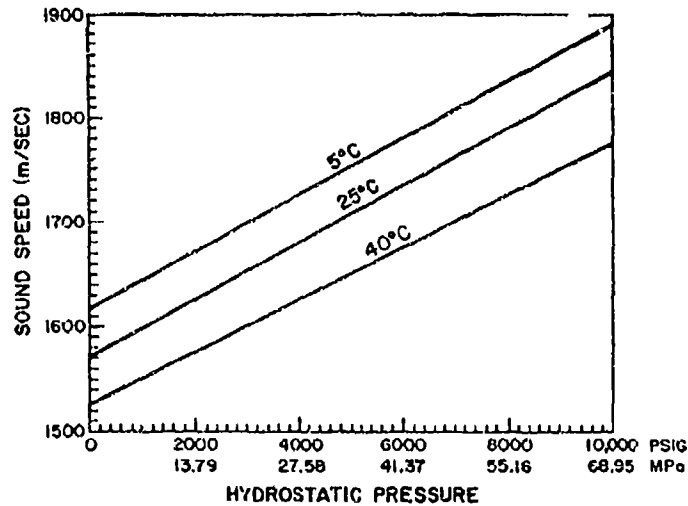


Fig. 5.3 - Longitudinal wave speed at 7 kHz as a function of temperature and pressure for Chlorobutyl H862A

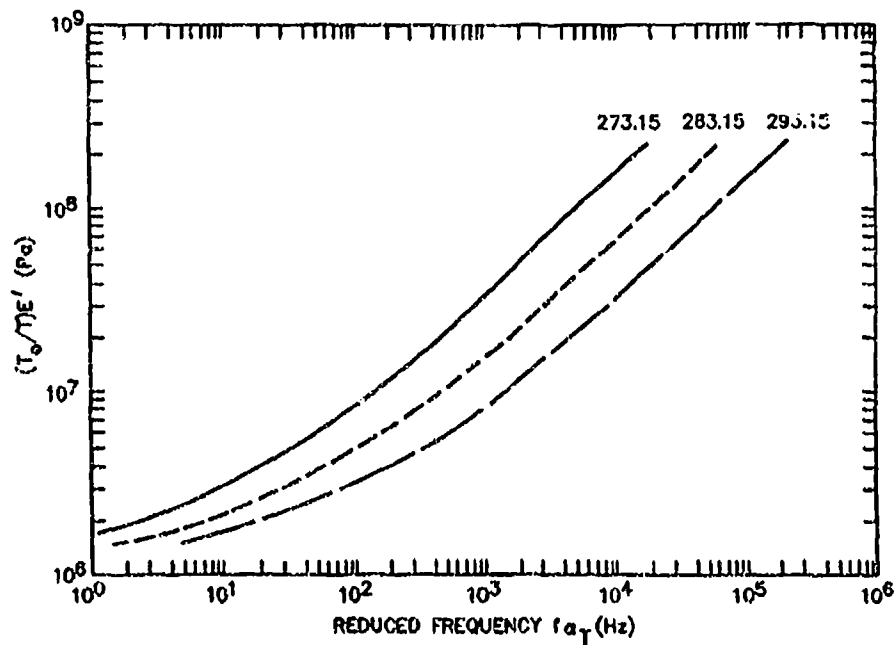


Fig. 5.4 - Plot of storage Young's modulus vs reduced frequency for Chlorobutyl H862A at three different temperatures

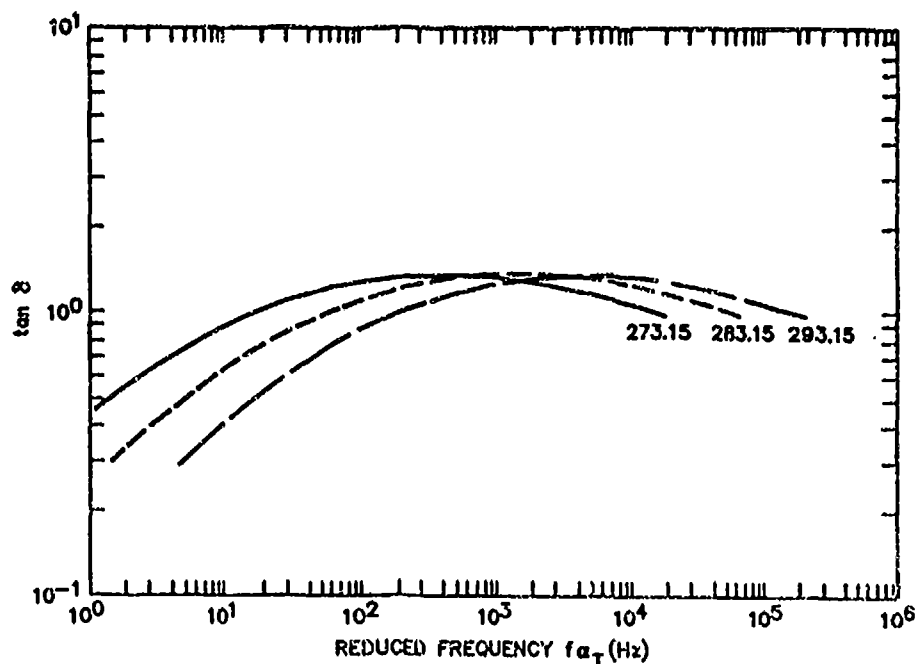


Fig. 5.5 - Plot of loss tangent vs reduced frequency for Chlorobutyl NS02A at three different temperatures

The physical parameters obtained for the four types of cure systems are summarized in Table 5.4. It can be seen that the red lead-ethylene thiourea and resin-cure systems have roughly equivalent hardness and tensile strengths, with the resin-cure system having greater ultimate elongation. Additionally, these systems had similar dynamic mechanical properties. This is illustrated in Figs. 5.6 and 5.7. Experimental points have been omitted to avoid obscuring the graph. All of this may be taken as evidence that the degree of crosslinking is similar in these systems, particularly since the Young's modulus will normally be an almost linear function of the degree of crosslinking. The mechanism of crosslinking of the red lead-ethylene thiourea cure presumably involves the formation of carbon-sulfur-carbon bonds as well as carbon-carbon bonds, while the brominated resin cure would involve the formation of carbon-oxygen linkages as well as carbon-carbon bonds. In contrast to these systems, the zinc-oxide, sulfur-donor-cure system gave vulcanizates with lower hardness values but greater tensile strengths and ultimate elongations. This is presumably due to the formation of other types of crosslinks than the other two systems^{312,317}. The litharge cure was somewhat anomalous in that the

material having no black did not crosslink satisfactorily. It is also interesting to note that the less reinforcing thermal black gave lower tensile strengths than the GPF black in all cases except for the zinc-oxide cure.

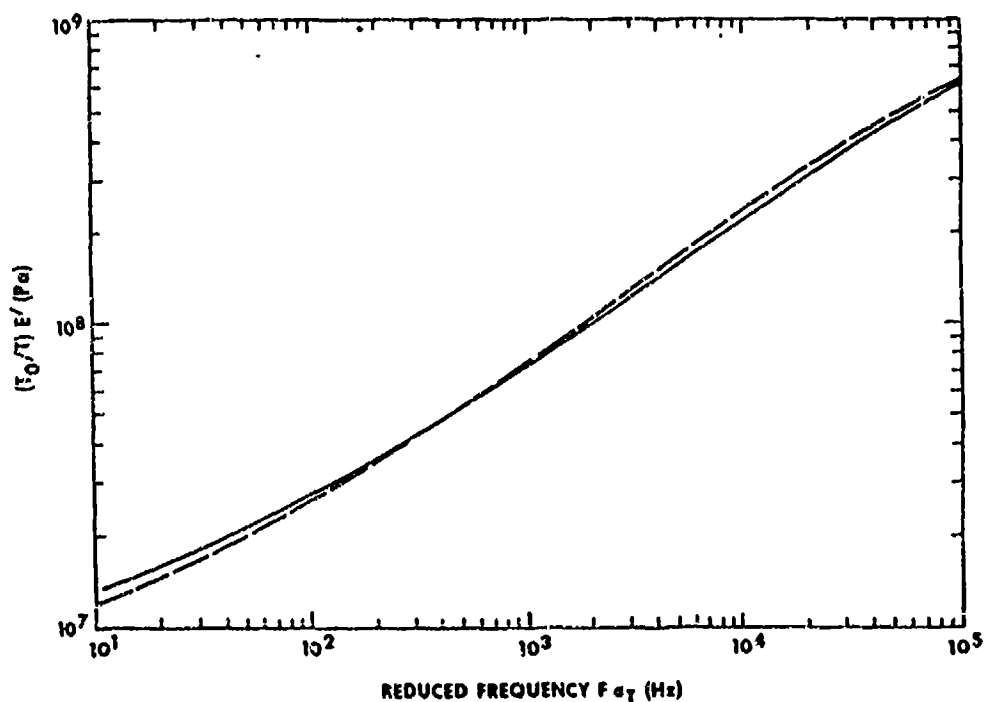


Fig. 5.6 - Plot of storage Young's modulus vs reduced frequency for red lead-cured (—) and resin-cured (---) chlorobutyls at 293.15K reinforced with 50 phr N660 black

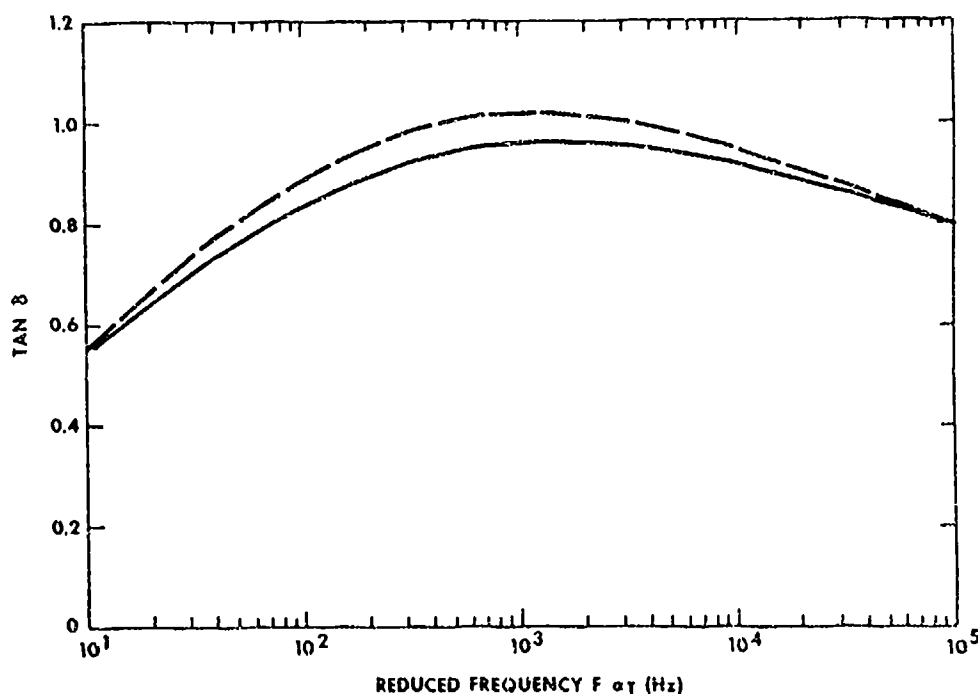


Fig. 5.7 - Plot of loss tangent vs reduced frequency for red lead-cured (—) and resin-cured (----) chlorobutyls at 288.15K reinforced with 50 phr N660 black

5.3 FILLERS

The choice of the type and amount of filler(s) to be used will depend on the hardness, tensile properties, electrical properties, and dynamic mechanical properties desired. Most practical butyl and chlorobutyl rubber compounds will contain from 35 to 100 phr of carbon black or as much as 100 to 150 phr of mineral fillers³¹². Blends of carbon black and mineral fillers can also be used to obtain the desired properties.

TABLE 5.4 - PHYSICAL PROPERTIES OBTAINED FROM FOUR DIFFERENT
CROSSLINKING SYSTEMS WITH NO BLACK AND 50-PHR LOADINGS OF
GPF (N660) BLACK AND MT (N990) BLACKS

Cure System	Type of Black	Tensile Strength (MPa)	Ultimate Elongation (%)	Density (kg/m ³)	Shore A Hardness
Red Lead	N660	9.84	310	1181	59
	N990	3.51	555	1182	44
	No black	1.42	360	1044	27

Zinc Oxide	N660	11.26	600	1212	48
	N990	12.10	895	1121	38
	No black	1.26	370	1007	24

Litharge	N660	9.70	350	1241	56
	N990	2.95	450	1151	39
	No black	-----DID NOT CROSSLINK-----			

Resin	N660	9.42	550	1124	56
	N990	4.44	480	1116	43
	No black	1.48	260	0966	27

Smaller sized carbon blacks typically give a greater degree of reinforcement; with higher tensile strength, Shore hardness, and higher Young's or shear storage modulus; and with lower loss tangent. The use of poly dinitrosobenzene in chlorobutyl stocks apparently exerts a type of leveling effect among carbon blacks over a limited particle size range^{309,320} (cf. Figs. 4.3 and 4.4, along with Table 5.5). Increased loading of a given type of black will lead to an increase in Shore A

hardness, a decreased electrical resistivity, a decrease in ultimate elongation, and an increase in tear strength. The frequency-dependent Young's modulus will increase, while the loss tangent will decrease (cf. Table 5.6 and Figs. 5.8 and 5.9).

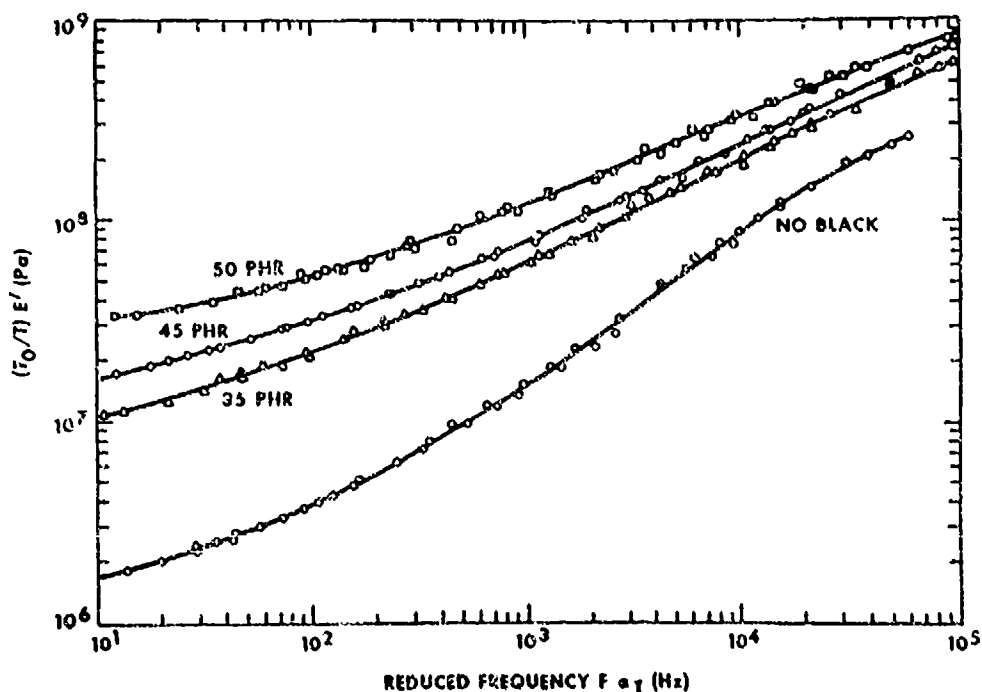


Fig. 5.8 - Plot of storage Young's modulus vs reduced frequency at 288.15K for resin-cured chlorobutyl reinforced with no black and three different loadings of N247 black

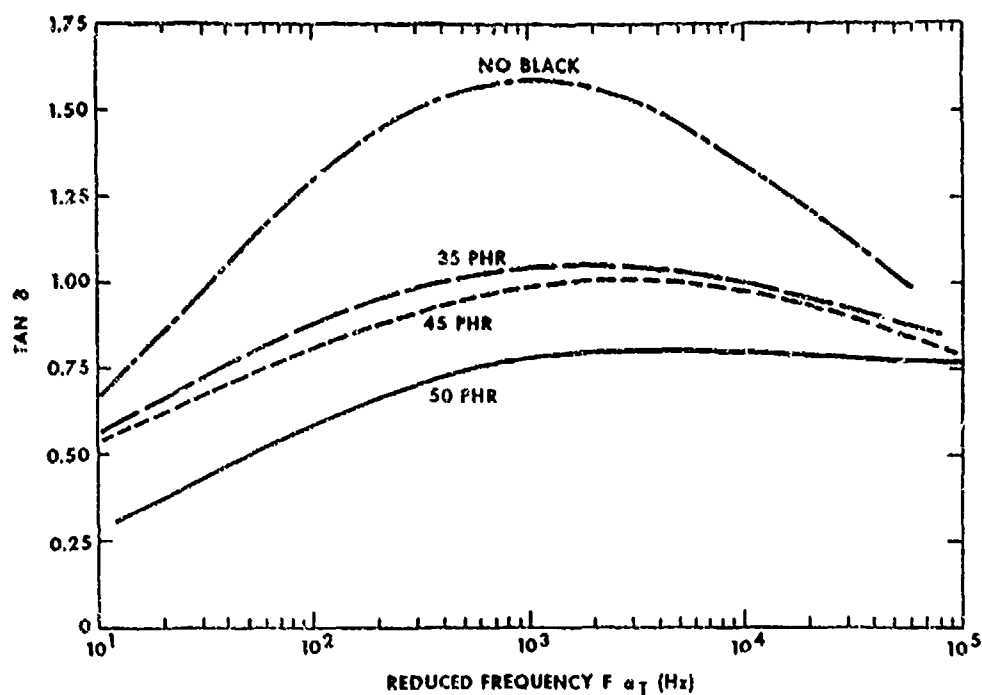


Fig. 5.9 - Plot of loss tangent vs reduced frequency at 293.15K for resin-cured chlorobutyl reinforced with no black and three different loadings of N847 black

TABLE 5.5 - PHYSICAL PROPERTIES OBTAINED FROM VARIOUS CARBON BLACKS AT 35-PHR LOADING IN RED LEAD-ETHYLENE THIOUREA CURE MODIFIED WITH 0.5-PHR POLY DNB AND 1-PHR ANTIOXIDANT 2246

Category of Black	Type of Black	Tear Strength (kN/m)	Tensile Strength (MPa)	Ultimate Elongation (%)	Density (kg/m ³)	Shore A Hardness
	None	8.75	1.26	290	1043	24
SAF	N110	37.6	10.3	290	1144	49
ISAF (LM)	N220	39.8	10.9	293	1132	55
ISAF (HM)	N234	39.0	6.05	205	1134	55
HAF-LS	N326	35.0	10.3	320	1132	51
HAF	N330	37.9	9.30	264	1134	49
HAF	N339	41.5	11.5	270	1137	56
HAF-HS	N347	39.5	10.6	260	1137	55
HAF-HS	N351	43.7	9.70	274	11420	50
FEF	N550	42.4	11.3	291	1143	53
FEF-LS	N539	39.8	9.00	330	1141	48
F...J	N650	36.2	7.65	300	1151	49
MT						
70 PHR	N990	22.8	3.88	510	1218	44
90 PHR	N990	24.9	4.10	486	1253	47

The use of HAF blacks in chlorobutyl formulations gives vulcanizates with good tensile and adhesive properties, particularly in the resin-cure system (Table 5.7). Evaluations of strips of this material bonded by Chemlock 205 primer and 234 and 238 adhesives, using the wet-static peel test described by Ting²⁷³, indicate that it possesses much superior bondability to the PB62A formulation.

TABLE 5.6 - SHIFT CONSTANTS AND POLYNOMIAL COEFFICIENTS FOR RESIN-CURED CHLOROBUTYL FORMULATIONS

Log a_T = Shift constant ($1/T - 1/T_0$)

Log (E' or $\tan \delta$) = $\sum a_n [\log \text{freq (Hz)}]^n$

<u>Coefficient</u>	<u>COMPOUND</u>		
	<u>B-10</u>	<u>B-11</u>	<u>B-14</u>
	<u>Modulus (283.15K)</u>		
a_0	5.82520	6.83612	7.46740
a_1	0.56153	0.12289	-0.030558
a_2	-0.27416	0.057468	0.065863
a_3	0.11734	0.007388	0.011157
a_4	-0.012721	-0.0018046	-0.0022899
	<u>Tan δ (283.15K)</u>		
a_0	-0.72106	-0.6041	-1.1052
a_1	0.68169	0.4400	0.77185
a_2	-0.14749	-0.09314	-0.18413
a_3	0.0075889	0.005225	0.014253
	<u>Shift Constant</u>		
	3829	4374	4158

The reinforcement of butyl and chlorobutyl by mineral fillers is similar to that produced by carbon blacks, but to a lesser degree. Mineral fillers tend to reduce tensile properties and compression-set resistance compared to carbon blacks. Use of mineral fillers such as mica will lead to a decrease in tensile properties (Tables 5.7 and 5.8) while causing an increase in the Young's modulus and a broadening in the loss tangent curve (Figs. 5.10 and 5.11, and Table 5.9).

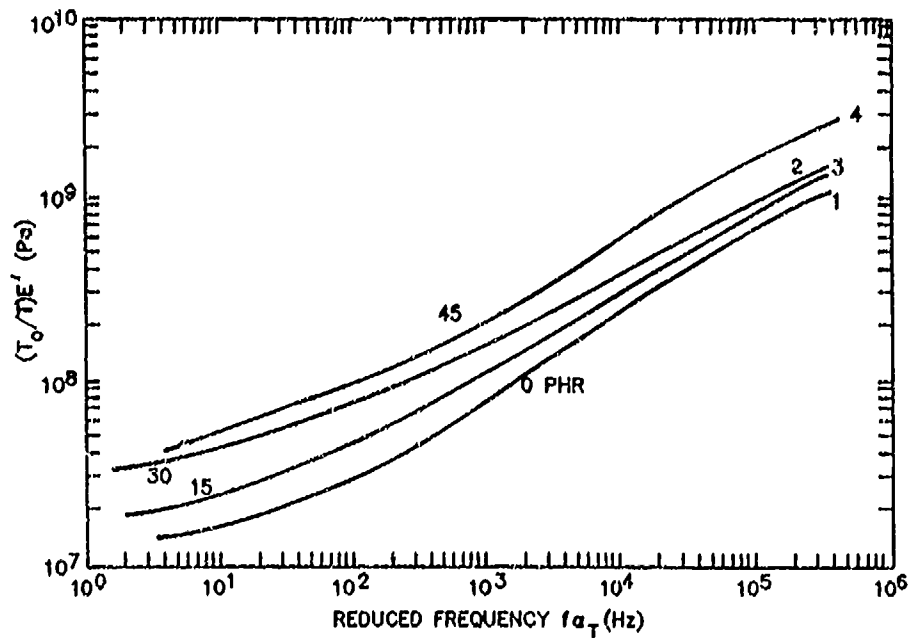


Fig. 5.10 - Plot of storage Young's modulus vs reduced frequency at 283.15K for resin-cured chlorobutyl with 35 phr N347 black and 0 phr of Mica (1) and different loadings of Mico-Mica C1000 (2 = 30 phr, 3 = 15 phr, 4 = 45 phr)

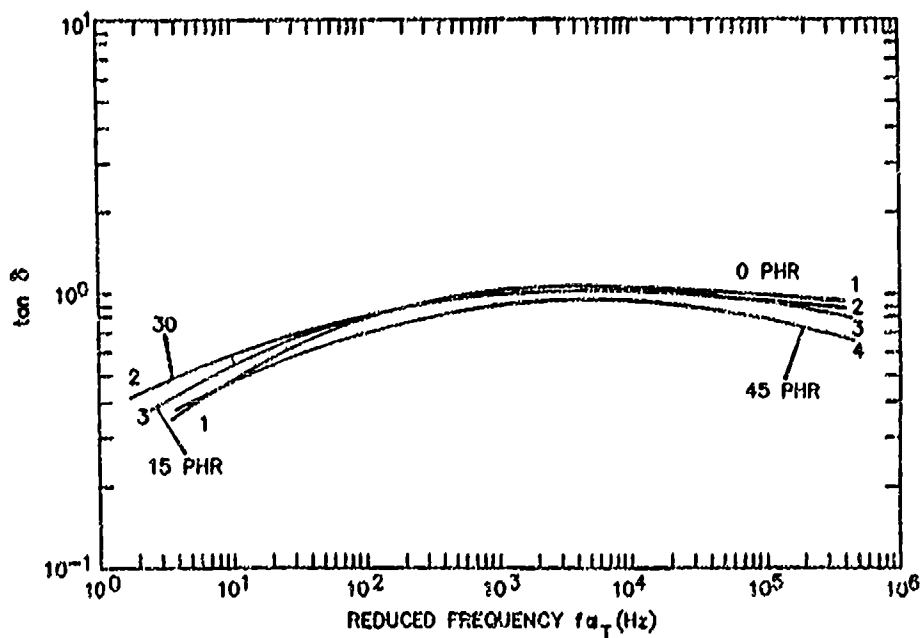


Fig. 5.11 - Plot of loss tangent vs reduced frequency at 283.15K for resin-cured chlorobutyl with 35 phr N347 black and 0 phr of Mica (1) and different loadings of Mico-Mica C1000 (2 = 30 phr, 3 = 15 phr, 4 = 45 phr)

TABLE 5.7 - FORMULATIONS AND REPRESENTATIVE PHYSICAL PROPERTIES OF RESIN-CURED CHLOROBUTYL AT VARYING LOADINGS OF N347 BLACK

FORMULATION:	B-10	B-11	B-14
COMPONENT	PHR		
Chlorobutyl HT1066	100.0	100.0	100.0
Philblack N347	0.0	35.0	50.0
Zinc Oxide	5.0	5.0	5.0
Schenectady SP1055	4.0	4.0	4.0
MBTS	2.0	2.0	2.0
Antioxidant 2246	1.0	1.0	1.0
Stearic Acid	1.0	1.0	1.0
Diphenylguanidine	0.5	0.5	0.5
Poly DNB	0.5	0.5	0.5
Total parts by weight:	114.0	149.0	164.0

STATIC PHYSICAL PROPERTIES:

PARAMETERS	VALUES			UNITS
Shore A Hardness	28	54	64	
Tensile Strength	2.53	16.2	16.5	MPa
Ultimate Elongation	503	623	473	%
200% Modulus	0.81	3.67	5.85	MPa
300% Modulus	1.21	6.63	10.05	MPa
Tear Strength	10.7	61.1	76.8	kN/m
Density	967.3	1081.3	1116.7	kg/m ³
Volume Resistivity	2x10 ¹⁵	9x10 ¹¹	7x10 ⁷	ohm·cm
Cure Temperature	155	155	155	°C
90% Cure Time	26	38	30	min.

TABLE 5.8 - FORMULATIONS AND REPRESENTATIVE PHYSICAL PROPERTIES OF
RESIN-CURED CHLOROBUTYL AT VARYING LOADINGS OF MYCA

FORMULATION:	SM-1	SM-2	SM-3	SM-4
COMPONENT	PHR			
Chlorobutyl HT1066	100.0	100.0	100.0	100.0
Vulcan 3H (N347)	35.0	35.0	35.0	35.0
Zinc Oxide	5.0	5.0	5.0	5.0
Schenectady SP1055	4.0	4.0	4.0	4.0
MBTS	2.0	2.0	2.0	2.0
Antioxidant 2246	1.0	1.0	1.0	1.0
Stearic Acid	1.0	1.0	1.0	1.0
Diphenylguanidine	0.5	0.5	0.5	0.5
Poly DNB	0.6	0.6	0.6	0.6
Micro-Nica C1000	0.0	30.0	15.0	45.0
Total parts by weight:	149.1	179.1	164.1	194.1

STATIC PHYSICAL PROPERTIES:

PARAMETERS	VALUE				UNITS
Shore A Hardness	54	62	56	65	
Tensile Strength	14.1	11.8	13.6	10.1	MPa
Ultimate Elongation	645	612	634	592	%
200% Modulus	3.58	3.85	3.68	3.61	MPa
300% Modulus	5.96	5.68	5.93	5.09	MPa
Tear Strength	62.4	54.8	58.1	48.0	kN/m ³
Density	1081.3	1180.4	1122.1	1260.5	kg/m ³
Log Vol. Res.	6.48	6.82	6.93	8.32	ohm-cm
Cure Temperature	155	155	155	155	°C
90% Cure Time	30	30	32	34	min.

TABLE 5.9 - SHIFT CONSTANTS AND POLYNOMIAL COEFFICIENTS FOR
MICA-FILLED CHLOROBUTYL FORMULATIONS

Log a_T = Shift constant ($1/T - 1/T_0$)

Log (E' or $\tan \delta$) = $\sum a_n [\log \text{freq (Hz)}]^n$

<u>Coefficient</u>	<u>Compound</u>			
	<u>SM-1</u>	<u>SM-2</u>	<u>SM-3</u>	<u>SM-4</u>
	<u>Modulus (283.15K)</u>			
a_0	7.17029	7.4970	7.2516	7.4301
a_1	-0.063461	0.059897	0.031059	0.35065
a_2	0.132065	0.066826	0.1025	-0.10116
a_3	-0.0061811	-0.0017025	-0.0082845	0.03937
a_4	-0.0007897	-0.00044894	-0.00036479	-0.0037677
	<u>Tan δ (283.15K)</u>			
a_0	-0.70107	-0.44677	-0.56235	-0.58828
a_1	0.48669	0.26108	0.37362	0.3084
a_2	-0.10437	-0.041928	-0.07581	-0.043319
a_3	0.0069407	0.0012287	0.0045199	0.00030267
	<u>Shift Constant</u>			
	4058	5290	4620	4398

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CHAPTER 6

ETHYLENE-PROPYLENE-DIENE MONOMER (EPDM)

6.1 GENERAL INFORMATION

Ethylene-propylene diene (EPDM) is a terpolymer based upon ethylene, propylene, and a controlled amount of a nonconjugated diene. Cyclic dienes (such as dicyclopentadiene and ethyldiene norbornene) or aliphatic dienes (such as 1,4 hexadiene) are normally chosen as the nonconjugated diene component³²¹. The unsaturation remaining after the initial synthesis is pendant to the main chain and permits classical sulfur vulcanization. This is normally in the range of 0.6- to 1.0-mole percent diene. If an aliphatic diene is used, it should contain only one terminal double bond to prevent cyclization and ensure that one side chain cure site is present for each molecule of diene in the terpolymer³²¹. For cyclic dienes, the double bond in the bicyclic ring is more reactive during polymerization. The remaining double bond, whose location is dependent upon the diene chosen, will be present in the side chain of the polymer. Its reactivity will be affected by the types of chemical structures adjacent to it. The copolymer portion of the elastomer is normally vulcanized by peroxide. The best physical properties are obtained when a small amount of a curing coagent such as sulfur, ethylene dimethacrylate, or polybutene is added. The coagent regulates the number of free radicals generated by the peroxide and improves the efficiency of the crosslinking reaction³²¹.

The elastomer class is a fairly new one and is considered a general-purpose synthetic elastomer with outstanding resistance to ozone and weathering, making it suitable for electrical applications. With suitable compounding, its dielectric constant and resistivity are high enough for insulation purposes. Appropriate compounding also gives good high-temperature performance. This class of materials also has good low-temperature flexibility (low-temperature stiffening point of -20 to -50°F (Ref. 4)). Ethylene-propylene diene also has good resistance to superheated steam and hot water, as well as many acids and alkalis, ketones, alcohols, and hydraulic fluids. It has poor resistance to oils, aromatic and aliphatic hydrocarbons, and chlorinated solvents.

Physical properties of EPDM are not as good as those of NR. Tear resistance is generally poorer, while tensile strength is comparable. Compression set resistance is less than NR. Bonding of EPDM is more difficult, particularly to metals. The EPDM compounds can be widely formulated, yielding compounds with either high or low hysteresis for damping and resilience, respectively.

Ethylene-propylene diene compounds are used commercially in the automotive industry. Typical applications include hoses, body mounts and pads, O-rings, wire and cable covers, weather stripping, and other areas requiring excellent weather resistance.

6.2 SPECIFIC FORMULATIONS

Some EPDM formulations that were specifically formulated for low hysteresis were developed at USRD³²² for evaluation as transducer window materials. Initial formulations were based upon both Nordel 1070 and Royalene 521. Nordel 1070 is a general-purpose EPDM gum stock manufactured by DuPont. Nordel 1070 is used for mechanical and automotive goods. It is normally vulcanized by sulfur, zinc oxide, thiurams and dithiocarbamates, or peroxides, with thiazoles used as secondary accelerators³²³. Royalene 521 is an EPDM gum stock manufactured by the Uniroyal Chemical Div. of Uniroyal, Inc. It is a relatively fast curing stock used for high-quality molded mechanical goods and wire and cable applications. Vulcanization systems are the same as used by Nordel. Both of these materials have low Mooney viscosities for easy processing.

The compositions and representative physical properties for some zinc-oxide, sulfur, and thiuram-cured Nordel compounds are given in Table 6.1. Table 6.2 gives similar information for some peroxide-cured Royalene 521 formulations. Although the Nordel produced slightly better tensile and tear properties than the Royalene, the Royalene was favored for use because it was easier to mold. Also, sulfur-based cures may lead to corrosion problems with silver electrodes in transducer applications.

TABLE 6.1 - EPDM NORDEL COMPOUNDS

FORMULATIONS:	<u>251-1</u>	<u>251-2</u>	<u>251-3</u>	
<u>COMPONENT</u>	<u>PHR</u>			
Nordel 1070	100.0	100.0	100.0	
N550 Black	35.0	40.0	45.0	
Chemlock 250	5.0	5.0	5.0	
Zinc Oxide	5.0	5.0	5.0	
Monex	1.0	1.0	1.0	
Stearic Acid	1.0	1.0	1.0	
Sulfur	1.0	1.0	1.0	
MBT	<u>0.25</u>	<u>0.25</u>	<u>0.25</u>	
Total parts by weight =	148.25	153.25	158.25	

STATIC PHYSICAL PROPERTIES:				
<u>PARAMETERS</u>	<u>VALUE</u>			<u>UNITS</u>
Shore A Hardness	58	60	59	
Tensile Strength	13.8	11.6	11.6	MPa
Ultimate Elongation	522	461	393	%
200% Modulus	4.33	4.57	4.57	MPa
300% Modulus	7.07	7.58	7.58	MPa
Tear Strength	49.1	51.6	51.6	kN/m
Density	1022.2	1043.8	1042.6	kg/m ³
Vol. Res.	1.41×10^{11}	2.50×10^{11}	1.15×10^{11}	ohm·cm
Cure Temperature	155	155	155	°C
90% Cure Time	45	54	44	min.

TABLE 6.2 - EPDM ROYALENE 521 COMPOUNDS

FORMULATIONS:	254-1	254-2	254-4
COMPONENT	PHR		
Royalene 521	100.0	100.0	100.0
N660 Black	40.0	45.0	55.0
DiCUP 40KE	6.0	6.0	6.0
Zinc Oxide	5.0	5.0	5.0
Sartomer SR350	2.0	2.0	2.0
Naugard Q	0.8	0.8	0.8
Total parts by weight =	153.8	158.8	168.8

PARAMETERS	VALUE			UNIT
Shore A Hardness	56	59	62	
Tensile Strength	9.54	12.4	13.9	MPa
Ultimate Elongation	337	394	322	%
200% Modulus	4.02	4.30	6.68	MPa
300% Modulus	7.84	8.04	12.4	MPa
Tear Strength	31.4	40.3	51.1	kN/m
Density	1044.3	1058.8	1081	kg/m ³
Vol. Res.	2.81×10^{12}	1.43×10^{11}	1.43×10^7	ohm·cm
Cure Temperature	155	155	155	°C
90% Cure Time	42	48	43	min.

The viscoelastic behavior of the Royalene compounds is depicted in Figs. 6.1 and 6.2 and Table 6.3. These materials possess relatively low losses over a wide frequency range and are similar to natural rubber compounds in their viscoelastic behavior.

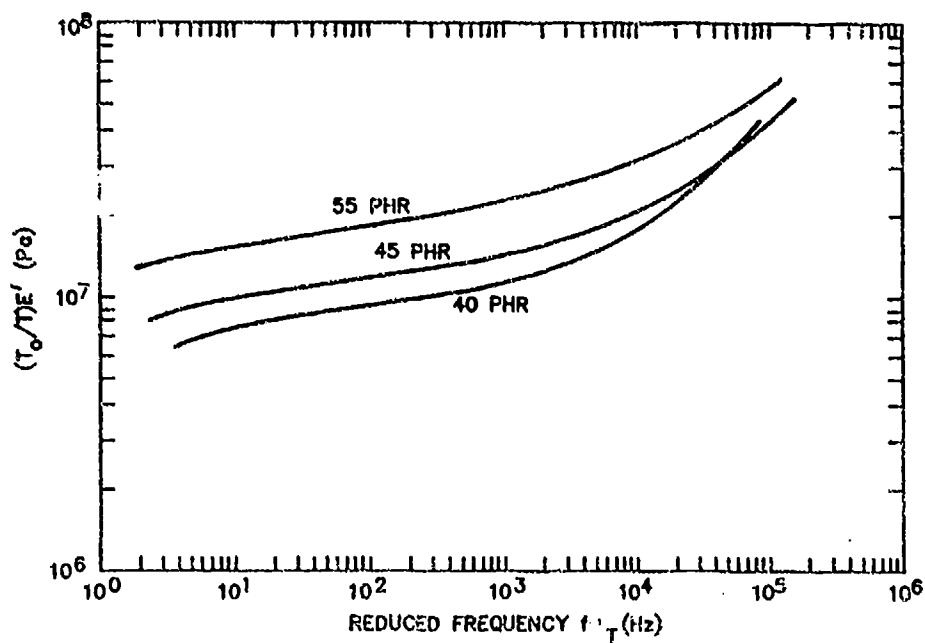


Fig. 6.1 - Plot of storage Young's modulus vs reduced frequency at 288.15K for peroxide-cured EPDM's at three different loadings of N660 black

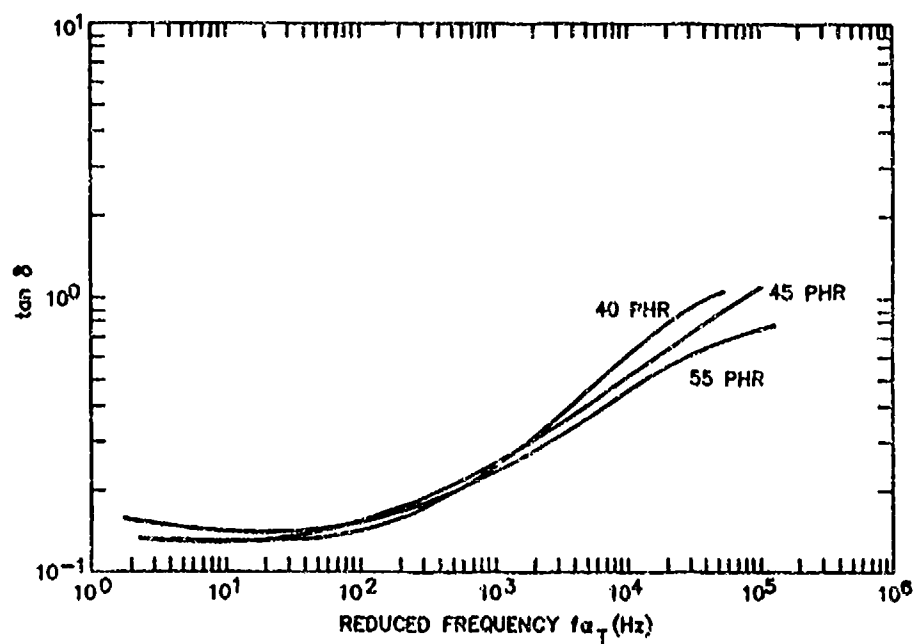


Fig. 6.2 - Plot of loss tangent vs reduced frequency at 288.15K for peroxide-cured EPDM's at three different loadings of N660 black

TABLE 6.3 - POLYNOMIAL COEFFICIENTS AND SHIFT CONSTANTS
FOR EPDM FORMULATIONS

$\text{Log } a_T = \text{Shift Constant } (1/T - 1/T_0)$

<u>Coefficient</u>	<u>COMPOUND</u>		
	<u>254-1</u>	<u>254-2</u>	<u>254-4</u>
	<u>Modulus (283.15K)</u>		
a_0	6.8145	6.9112	7.0967
a_1	0.029141	0.060308	0.072159
a_2	0.066034	0.033127	0.016278
a_3	-0.029087	-0.016576	-0.0087837
a_4	0.0043589	0.002654	0.0015841

	<u>Tan δ (283.15K)</u>		
a_0	-0.69197	-0.80470	-0.70623
a_1	-0.34170	-0.18577	-0.27706
a_2	0.15494	0.10667	0.13551
a_3	-0.010449	-0.007214	-0.0011222

Shift Constant

3820	4365	4804
------	------	------

The formulation listed in Table 6.4 was developed as a result of a study to improve the bondability, tear strength, and processing characteristics of the Royalene EPDM formulation³²². This involved an investigation of the effects of variations in the cure system (peroxide and coagent), carbon black loading, and antioxidant. The formulation in

Table 6.4 was touted as having the best all-around compromise among bondability to metals, tear strength, hardness, electrical resistivity, scorch time, and viscoelastic properties (Figs. 6.3 and 6.4).

TABLE 6.4 - EPDM FORMULATION 252-1

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
Royalene 521	100.0
N660 Black	45.0
DiCUP 40KE	5.0
Zinc Oxide	5.0
Sartomer SR350	2.0
Naugard Q	0.8

Total parts by weight = 157.8

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	60	
Tensile Strength	13.5	MPa
Ultimate Elongation	288	%
200% Modulus	7.30	MPa
Tear Strength	45.3	kN/m ₃
Density	1068.8	kg/m ³
Volume Resistivity	3.33×10^9	ohm·cm
Cure Temperature	155	°C
90% Cure Time	50	min.

$$\text{Log } a_T = 4270 (1/T - 1/T_0)$$

<u>Coefficient:</u>	<u>Modulus (283.15K)</u>	<u>tan δ (283.15K)</u>
a_0	6.9120	-0.7394
a_1	0.13023	-0.29042
a_2	-0.022050	0.15930
a_3	0.00086023	-0.013907
a_4	0.00096193	0.00

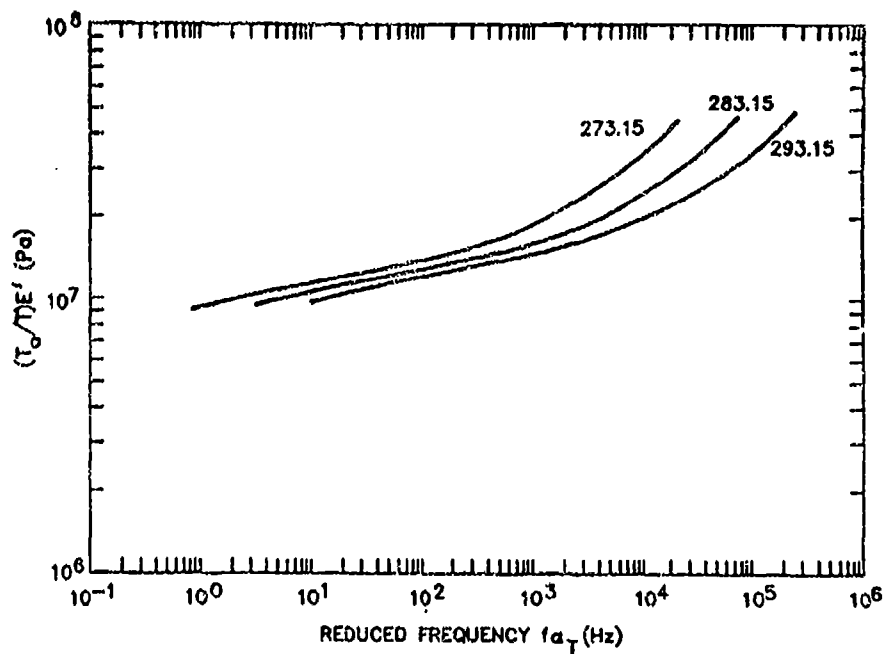


Fig. 6.3 - Plot of storage Young's modulus vs reduced frequency at three temperatures for optimized peroxide-cured EPDM

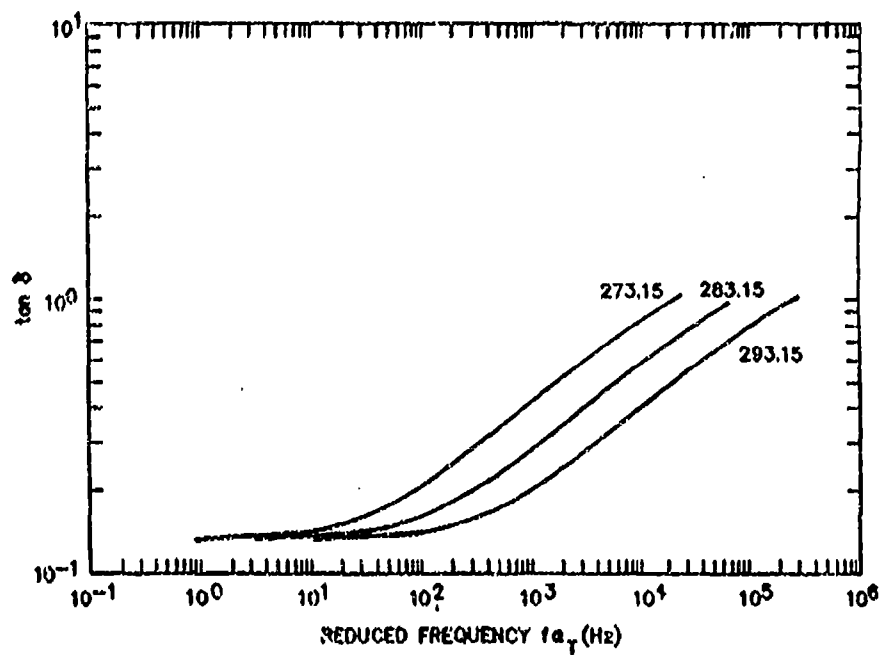


Fig. 6.4 - Plot of loss tangent vs reduced frequency at three temperatures for optimized peroxide-cured EPDM

An example of a different type of EPDM formulation is listed in Table 6.5. This material is compounded for use as a cable jacketing material, and possesses good electrical properties³²⁴. Compared to the earlier formulations discussed, this material also has relatively low loss³²⁵ (Figs. 6.5 and 6.6).

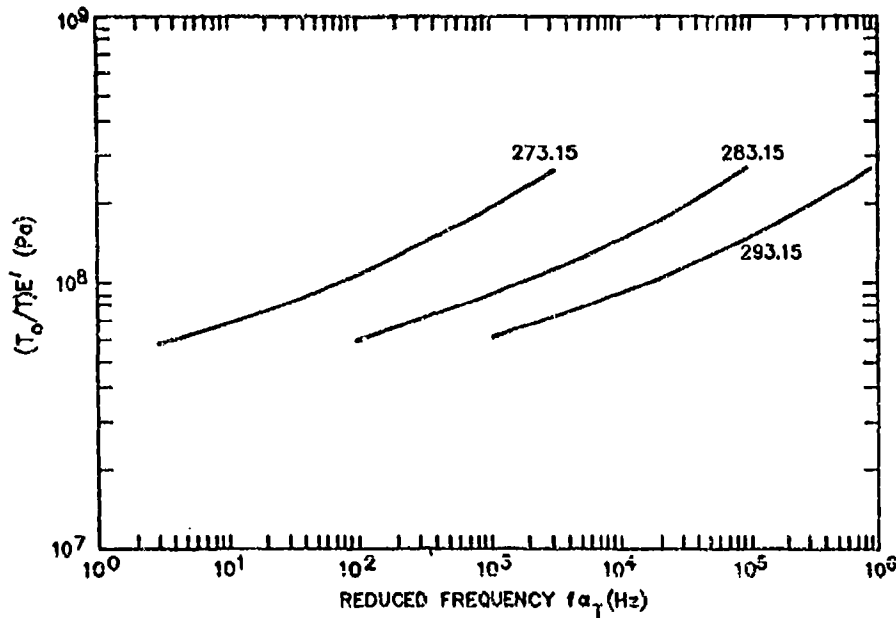


Fig. 6.5 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Royalene 466 EPDM

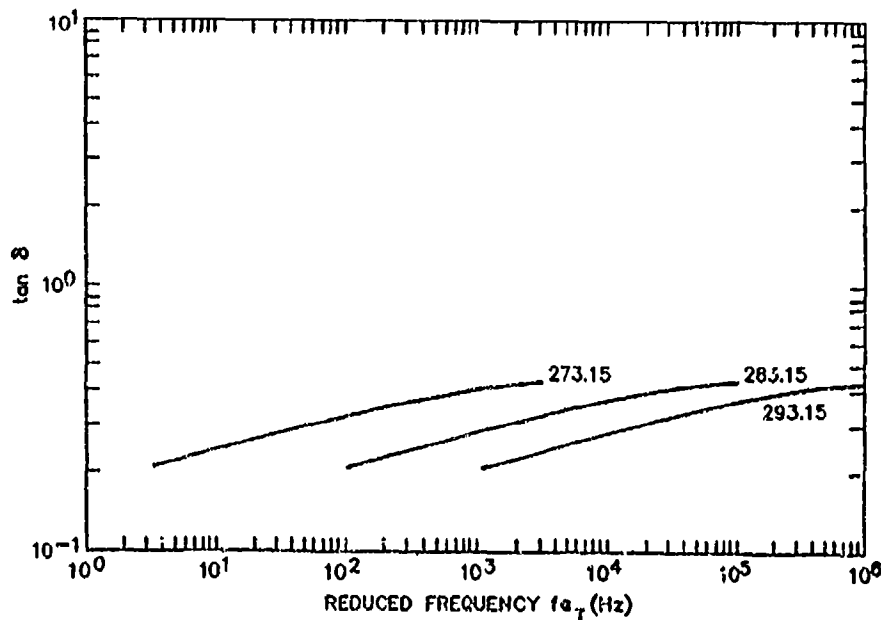


Fig. 6.6 - Plot of loss tangent vs reduced frequency at three temperatures for Royalene 466 EPDM

TABLE 6.5 - EPDM FORMULATION ROYALENE 400

FORMULATIONS:

<u>COMPONENT</u>	<u>PHR</u>
Royalene 400	120.0
Burgess KE Clay	200.0
MB X353	47.1
Paraffinic Oil	30.0
Red Lead	10.0
SRF Black	10.0
Zinc Oxide	10.0
DiCUP R	3.9
Dibenzo GMF	<u>1.0</u>

Total parts by weight = 432.0

The formulation for MB X353 is as follows:

<u>COMPONENT</u>	<u>PHR</u>
Royalene 400	20.0
Polyethylene	20.0
Burgess KE Clay	5.0
Dicumyl Peroxide	1.1
Trimethyldihydroquinoline (polymerized)	<u>1.0</u>

Total parts by weight = 47.1

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1381.0	kg/m ³
Cure Temperature	160	°C
90% Cure Time	25	min.

$$\text{Log } a_T = -8.60(T - 283.15) / (53.9 + T - 283.15)$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.17487	-0.81432
a_1	0.55676	-0.014121
a_2	-0.196382	0.052252
a_3	0.039739	-0.0062294
a_4	-0.0025511	0.00

CHAPTER 7

FLUOROCARBON RUBBERS (CFM)

7.1 GENERAL INFORMATION

Fluorocarbon elastomers (CFM) are synthetic elastomers that contain varying proportions of fluorine. The classes of materials marketed as Fluorel and Viton by 3M and DuPont, respectively, are copolymers of vinylidene fluoride and hexafluoropropylene. Kel-F, also marketed by 3M, is a copolymer of chlorotrifluoroethylene and vinylidene fluoride^{224,326,327}. It is used primarily for hoses and seals for JP fuels. Kalrez, marketed by DuPont, is a related perfluoroelastomer. However, it is normally sold only in finished part form. Due to the high cost of monomers used in Kalrez and the difficulty in fabrication, it is relatively expensive. Therefore, it should be considered for use in cases only where no other type of elastomer would meet the severe service requirements.

Fluorocarbon elastomers have excellent resistance to oils, fuels, lubricants, and most mineral acids. They also resist many aliphatic and aromatic hydrocarbons (benzene, toluene, xylene, carbon tetrachloride) that act as solvents for many other types of elastomers. They are not recommended for use in low molecular weight ethers or esters such as isopropyl ether or ethyl acetate. They are quite suitable for use with organically derived oils such as castor or linseed oils. They may show some deterioration³²⁸ after exposure to paraffinic solvents at high temperatures or over long periods of time.

Viton itself is relatively impermeable to air and other gases, with a permeability about midway between the best and worst types of elastomers³²⁸. The permeability may be modified by compounding but will increase with increasing temperature in all cases.

Fluorocarbon elastomers have excellent resistance to atmospheric oxidation, ozone, and ultraviolet radiation. Electrical properties of these materials make them suitable for use as insulation at low frequencies and low voltages. Fluorocarbon elastomers also possess excellent abrasion resistance and good compression set and heat resistance.

Vulcanization of this class of materials is normally initiated by a basic material such as magnesium oxide, which also acts as an acid neutralizer for hydrogen fluoride that is formed^{326,327}. Crosslinking is carried out by difunctional amines. Commercially used materials are normally blocked amines to give greater processing safety. These materials are^{323,328,327}: hexamethylene diamine carbamate (HMDA-C or Diak #1) used in the range of 0.75 to 1.5 phr; ethylene diamine carbamate (Diak #2) used in the range of 0.85 to 2.5 phr; N, N'-dicinnamylidene 1,6 hexane-diamine (Diak #3) used in the range of 2 to 4 phr; and Diak #4, which is an alicyclic amine salt in the usual range of 1.9 to 2.4 phr. Disalicyl propylene diamine (copper inhibitor 50) is also used as a secondary curing agent in the range of 0.2 to 1 phr. Cure time is normally 30 min. at 150°C, with a 24-hr oven post-cure at 210°C to develop optimum properties.

Fluorocarbon elastomers are capable of good bonding to metals with the proper choice of adhesive³²⁶. Diak #1 is normally the curative of choice to promote successful adhesion. Diak #3 may also be used, but the amount of copper inhibitor #50 used should be minimal.

7.2 SPECIFIC FORMULATIONS

The viscoelastic properties typically obtained from several Viton formulations are shown in Figs. 7.1 through 7.5. The composition and typical physical properties of a Viton A formulation are given in Table 7.1^{224,298}. Viton A is a copolymer of hexafluoropropylene and vinylidene fluoride. The formulation in Table 7.1 is similar to that typically used for molded/extruded O-rings, gaskets, and seals.

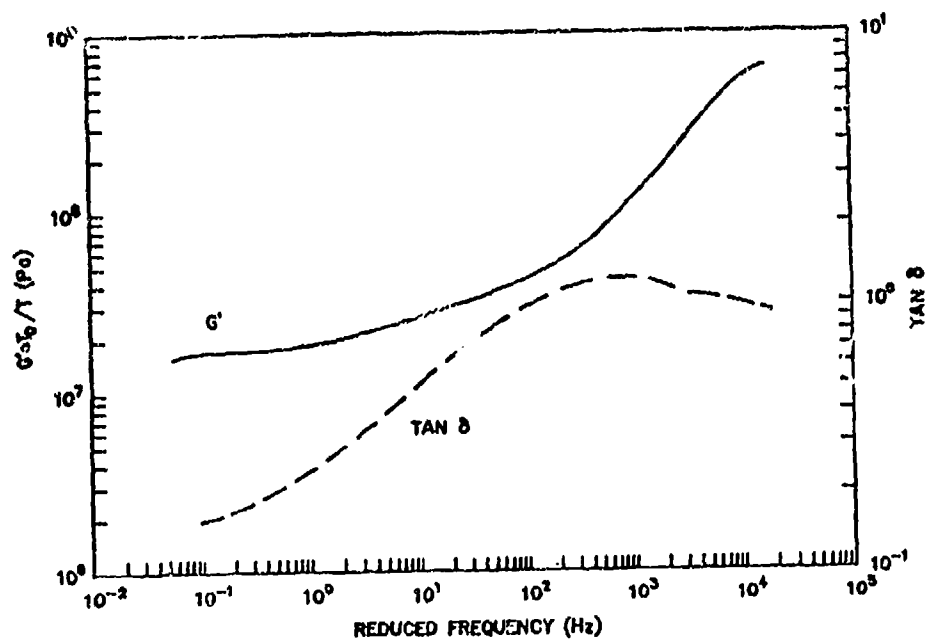


Fig. 7.1 - Plot of shear storage modulus (—) and loss tangent (----) vs reduced frequency at 295.85K for Viton A

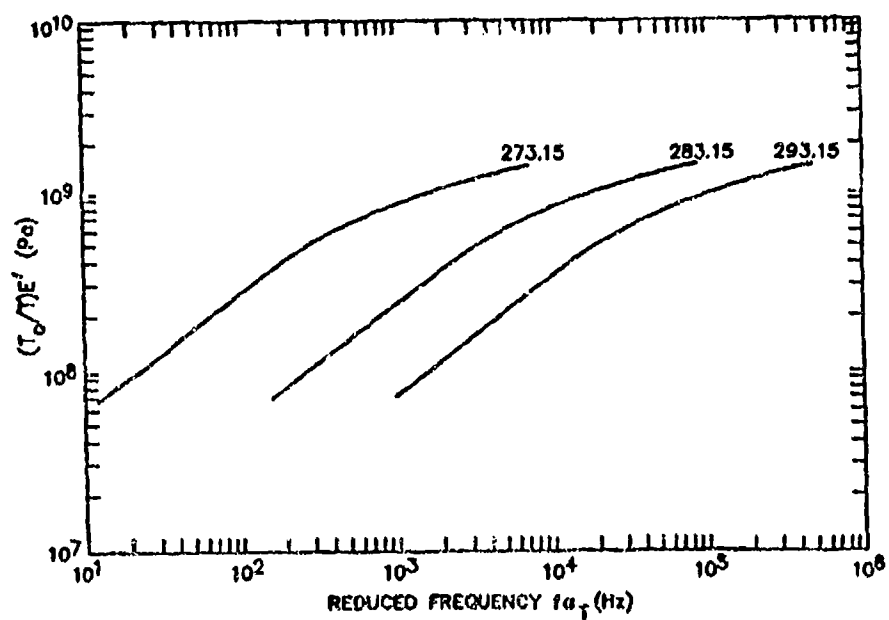


Fig. 7.2 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Viton B-50

Two other fluoroelastomer formulations are given in Table 7.2. The Viton B series is formulated to have better heat and fluid resistance than the A type. Viton B-50 is normally used for extruded products and complicated moldings. Viton B-910 is a Viton B with curing chemical incorporated. The viscoelastic properties³²⁵ of these materials are depicted graphically in Figs. 7.2 through 7.5.

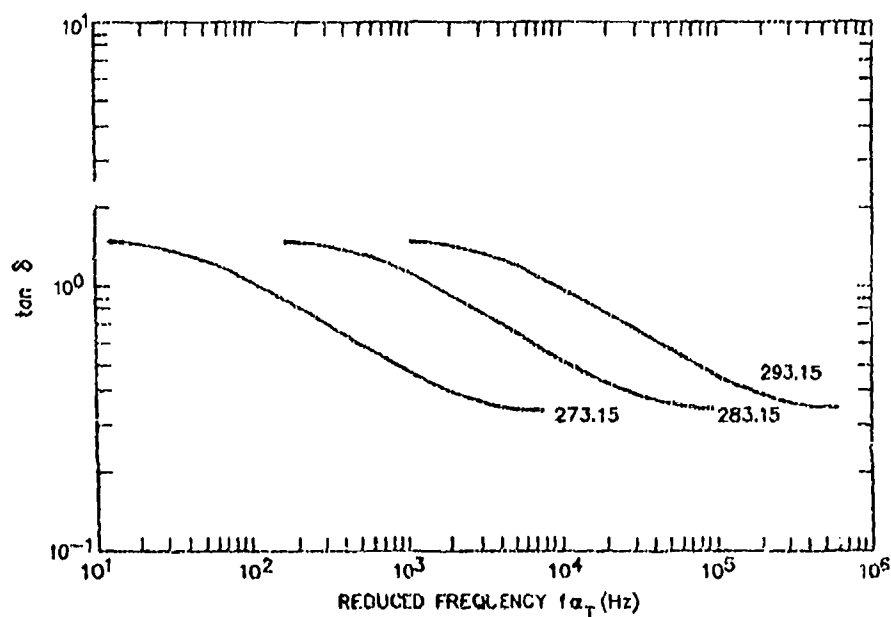


Fig. 7.3 - Plot of loss tangent vs reduced frequency at three temperatures for Viton B-50

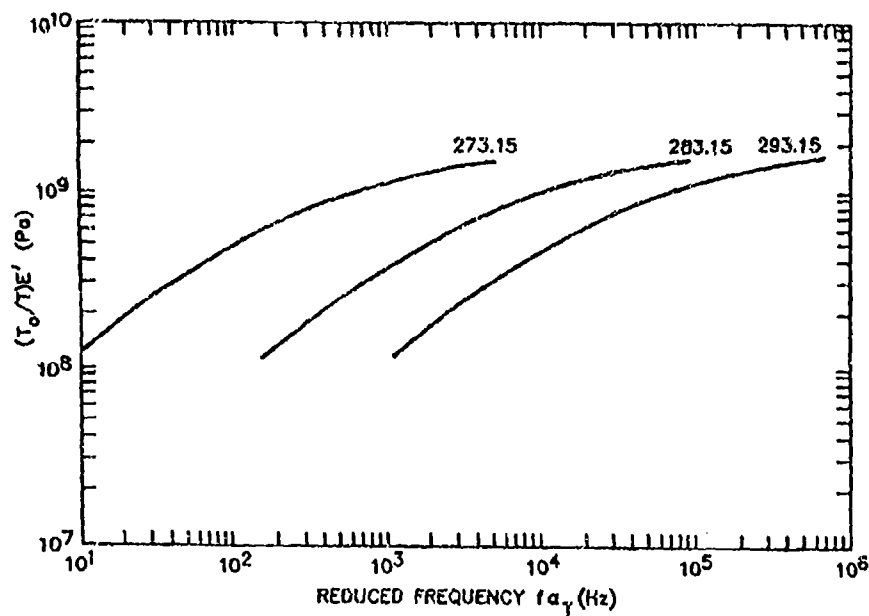


Fig. 7.4 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Viton B-916

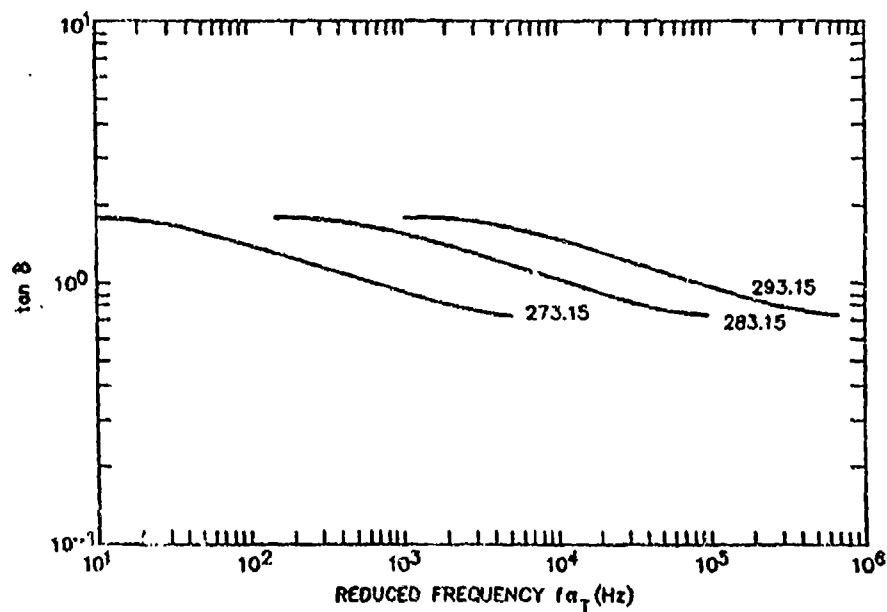


Fig. 7.5 - Plot of loss tangent vs reduced frequency at three temperatures for Viton B-916

TABLE 7.1 - VITON A FORMULATION

<u>COMPONENT</u>	<u>PHR</u>
Viton A	100.0
MT Carbon Black	18.0
Magnesium Oxide	15.0
Ethylenediamine Carbamate	<u>1.0</u>
Total Parts By Weight = 134.0	

<u>TYPICAL STATIC PHYSICAL PROPERTIES</u>	<u>VALUE</u>	<u>UNITS</u>
Tensile Strength	16.9	Mpa
100% Modulus	7.2	Mpa
Ultimate Elongation	160	%
Shore A Hardness	75	
Density	1790	kg/m ³
Low Temp. Stiffness	-35	°C
Water Permeability (10 ⁻¹⁰ g H ₂ O cm/cm ² -hr-torr)	520	
Cure Time	60	min.
Cure Temperature	150	°C
Post-Cure Temperature	200	°C
Post-Cure Time	24	hrs.

$$\text{Log } a_T = -11.0(T - 298.15) / (128 + T - 298.15)$$

<u>Coefficient</u>	<u>Modulus (298.15K)</u>	<u>Tan δ (298.15K)</u>
a_0	7.27594	-0.622614
a_1	0.099949	0.26839
a_2	0.834599	0.079856
a_3	-0.0157521	-0.020351
a_4	-0.024467	-0.0081097
a_5	0.01481241	0.0016017
a_6	-0.0019918	0

TABLE 7.2 - VITON B FORMULATIONS

FORMULATION B-50:

<u>COMPONENT</u>	<u>PHR</u>
Viton B-50	100.0
Carbon Black MT	20.0
Maglite Y	15.0
Diak No. 3	<u>3.0</u>

Total parts by weight = 138.0

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1895.0	kg/m ³
Cure Temperature	169	°C
90% Cure Time	15 - 20	minutes
Post cure for 24 hrs. at 204°C		

$$\log a_T = -5.60(T - 283.15) / (59.5 + T - 283.15) \quad (\text{Ref. 325})$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	10.2785	-1.6488
a_1	-4.1740	1.9217
a_2	2.1826	-0.62714
a_3	-0.41555	0.057954
a_4	0.027498	0

(continued)

TABLE 7.2 (Continues)

FORMULATION B-910:

<u>COMPONENT</u>	<u>PHR</u>
Viton B-910	100.0
Carbon Black MT	30.0
Calcium Hydroxide	3.0
Maglite D	<u>3.0</u>

Total parts by weight = 136.0

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1840.0	kg/m ³
Cure Temperature	177	°C
90% Cure Time	5	minutes
Post cure 24 hrs. at 204°C		

$$\text{Log } a_T = -5.17(T - 283.15) / (50.5 + T - 283.15) \quad (\text{Ref. 325})$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.7464	-0.25991
a_1	-0.90602	1.10187
a_2	0.79606	-0.32216
a_3	-0.16756	0.028006
a_4	0.011278	0

CHAPTER 8

NATURAL RUBBER (NR)

8.1 GENERAL INFORMATION

Practically all natural rubber (ASTM D1418 designation NR) used today is the coagulated latex of the rubber tree *Heavea brasiliensis*, although there is currently renewed interest in the latex of the guyuale shrub³²⁹. Its principal polymeric component is cis-polyisoprene. The natural emulsion contains about 35% colloidal polymer molecules that are stabilized by natural surfactants in the latex. Additionally, the latex contains about 5% of miscellaneous organic materials.

The grade of the latex is determined by the extent of removal of this organic matter during the coagulation process, plus the incorporation of other foreign material such as dirt or bark. Many grades and types of NR are available. There are 35 standard international grades of dry natural rubber³³⁰. These are divided into eight types, with each type referring to the source of the rubber and the manner in which it is prepared. A more complete discussion of this is given in Ref. 330.

Natural rubber is the general-purpose elastomer by which all synthetic elastomers are judged. It is considered to be the best general purpose rubber, embodying characteristics and properties suitable for a broad range of engineering applications. It is the best choice for many applications except those where an extreme performance or environmental requirement necessitates the use of a special-purpose elastomer.

Natural rubber is a very resilient material, with a large capacity for deformation. Additionally, its ability to strain crystallize gives it added strength upon deformation. It is therefore a good candidate for shock and severe dynamic load applications. Properties that are negatively affected³¹¹ by heat (such as flex, cut, and abrasion resistance) can be greatly improved through proper compounding. Natural rubber has low compression set and stress relaxation, making it suitable for sealing applications. It also has excellent general-processing characteristics.

Natural rubber is limited in its temperature range of applicability, compared to special-purpose elastomers such as silicone. However, its useful range of application in most compounded stocks will range from about -60 to about +200°F. Other notably poor characteristics of NR (such as resistance to oils, hydrocarbon, or chlorinated solvents, oxidation, and ozone resistance) can be minimized through proper compounding or part design. Natural rubber remains the best choice for many commercial applications, such as tires, mountings, seals, isolators, springs, and other dynamic applications.

8.2 CURE SYSTEMS

Natural rubber can be crosslinked by a variety of cure systems. Historically, the most important of these has been sulfur vulcanization. Improvements in the sulfur cure were realized with the advent of amine accelerators³³¹. Most sulfur-based cure systems for NR contain 2 to 7 phr of sulfur, 1 to 3 parts of primary accelerator, and smaller amounts of secondary accelerators. A cure activator [consisting of about 5 phr of a metallic oxide (zinc or lead) and a fatty acid such as stearic] is normally used. Lead oxide typically gives a faster rate of cure, with greater reversion resistance. Antioxidants and fillers (particularly carbon black) are usually added for better environmental resistance and improved physical properties.

Other curatives include sulfur donors, such as dimorpholinyl disulfide or MBTS³³¹. These cures typically have very good resistance to natural and accelerated aging. However, their flex-cracking resistance is much poorer than that obtained by elemental sulfur cures. Sulfurless curing agents that have been used for NR include both free-radical generators and bifunctional organic reagents. Dicumyl peroxide is one of the more commonly used free-radical generators, with good aging properties and flex-cracking resistance intermediate between that of sulfur and sulfur donor cures. Bifunctional organic reagents that have been used include benzoquinone dioxime in the presence of oxidizing Pb_3O_4 . m-Dinitrobenzene, in combination with PbO , has also been used. For further combinations of cure systems, it is suggested that the reader consult Refs. 224, 323 and 332.

TABLE 8.1 - MINSY NATURAL RUBBER

FORMULATION:	AA 165-4	AA 165-5	AA 165-6	
COMPONENT	PHR			
Smoked Sheet	100.0	100	100	
Huber N-860	40.0	8	65	
Protox 168	5.0	5.0	5.0	
Circo LP Oil	3.0	3.0	3.0	
Octamine	2.0	2.0	2.0	
Sulfur	1.5	1.5	1.5	
Altax	1.0	1.0	1.0	
Stearic Acid	1.0	1.0	1.0	
Unads	0.3	0.3	0.	
Total part by weight =	153.8	119.8	178.8	
STATIC PHYSICAL PROPERTIES:				
PARAMETERS	VALUE			UNITS
Shore A Hardness	50	35	64	
Tensile Strength	21.0	17.4	18	Pa
Ultimate Elongation	560	710	420	%
300% Modulus	6.82	1.52	13.0	MPa
Density	1095	990.0	1165	kg/m ³
Cure Temperature	155	155	155	°C
90% Cure Time	15	15	15	min.
Log a_T = Shift Constant ($1/T - 1/T_0$)				
Coefficient	Modulus (283.15K)			
a_0	6.39244	6.1183	6.727	
a_1	-0.00605984	-0.070940	0.14574	
a_2	0.0867265	0.11964	-0.02617	
a_3	-0.0318720	-0.043413	0.008867	
a_4	0.00499208	0.0067797	-0.00034891	
	Tan δ (283.15K)			
a_0	-0.96554	-0.81456	-0.79290	
a_1	-0.036942	-0.54046	0.37178	
a_2	0.11181	0.35967	0.0037273	
a_3	-0.012419	-0.044629	-0.010152	
Shift Constants:	4026	3412	4201	

TABLE 8.2 - DTNSRDC 334-291 NATURAL RUBBER

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
SMR-5	100.0
Thermax N-990	20
Protox 166	5.5
Circo LP Oil	18.0
Octamine	2.0
Sulfur	1.5
Altax	1.0
Stearic Acid	1.0
Unads	<u>0.3</u>

Total parts by weight = 150.3

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	34	
Density	1018.4	kg/m ³
Cure Temperature	155	°C
90% Cure Time	12	min.

$$\log a_T = 2955 (1/T - 1/283.15)$$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	5.8177	-0.87445
a_1	0.49336	-0.56674
a_2	-0.29856	0.42334
a_3	0.076098	-0.043649
a_4	-0.00049637	0

8.3 SPECIFIC FORMULATIONS

The compositions and typical physical properties of some sulfur-cured NR compounds³³³ are given in Tables 8.1 and 8.2. Examination of Table 8.1 shows that increased loading of carbon black causes an increase in Shore A hardness. The tensile strength shows little variation with changes in carbon black loading, while the ultimate elongation decreases. Increased carbon black loading causes an increase in the 300% modulus.

Compared to other classes of elastomers such as chlorobutyl, these materials exhibit low hysteresis and are relatively resilient. Increased loading of the same type of black causes an increase in the storage Young's modulus and a decrease in the loss tangent as a function of frequency³³³ (cf. Figs. 8.1 through 8.6). Use of a weakly reinforcing MT black gives a material with a relatively low modulus and higher loss (Figs. 8.7 and 8.8).

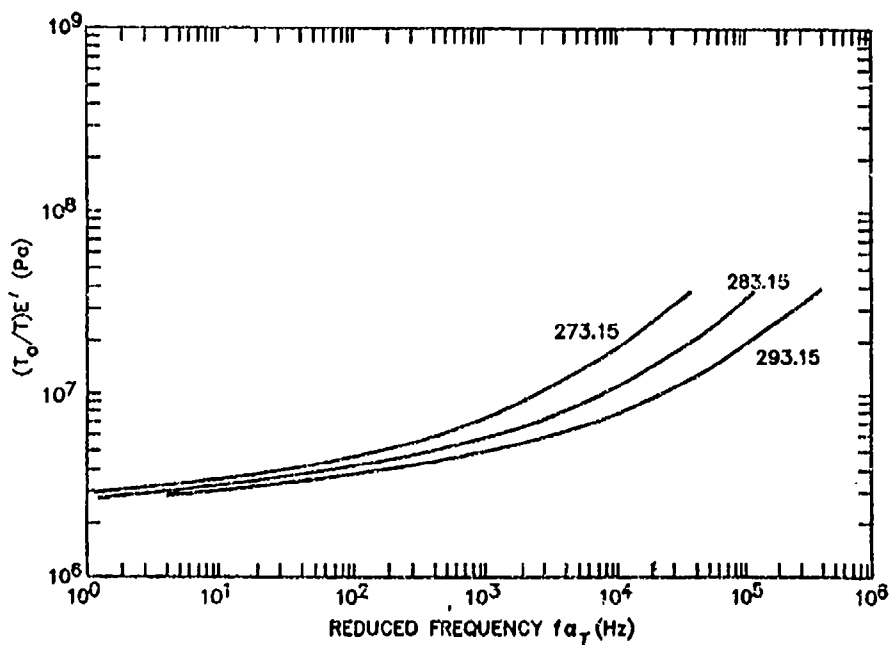


Fig. 8.1 -- Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-4

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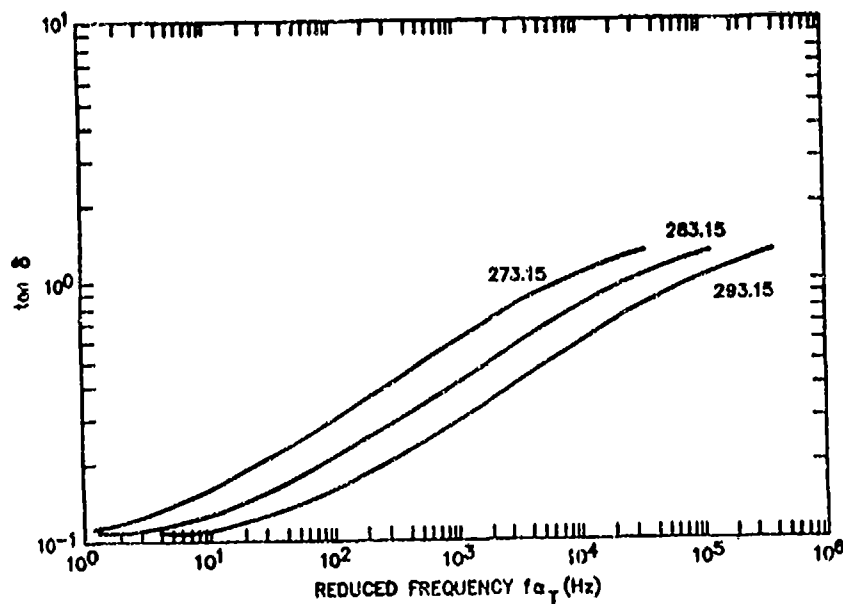


Fig. 3.2 - Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 165-4

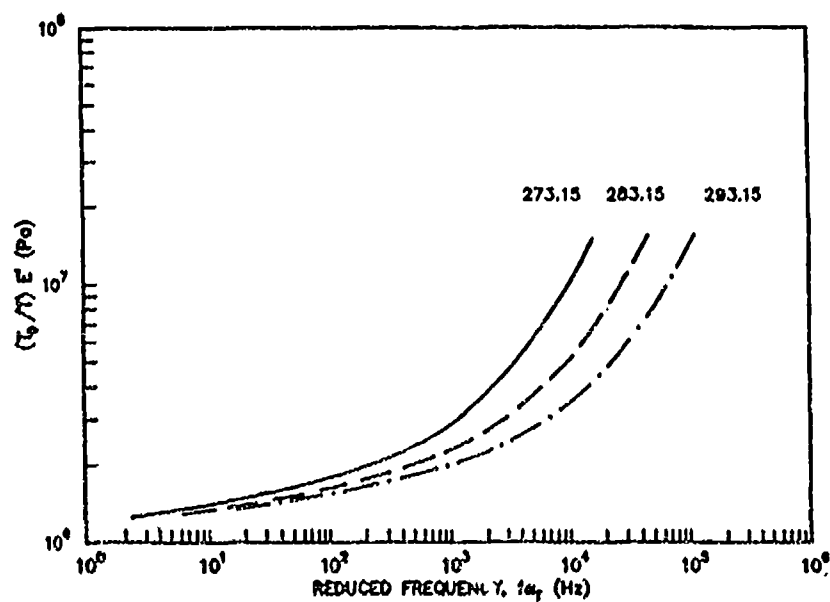


Fig. 3.3 - Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-5

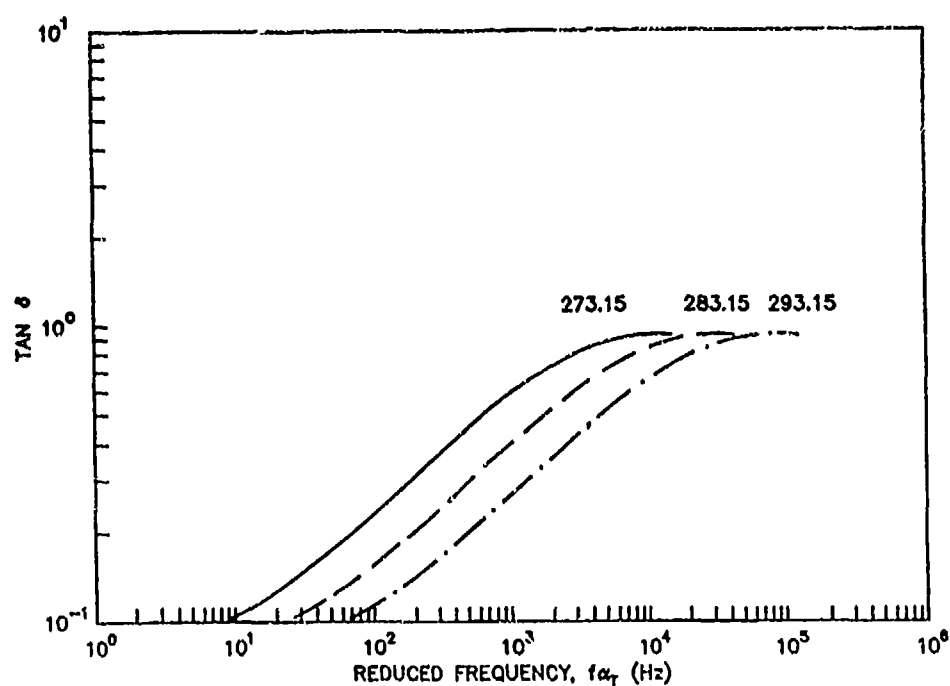


Fig. 8.4 - Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 165-5

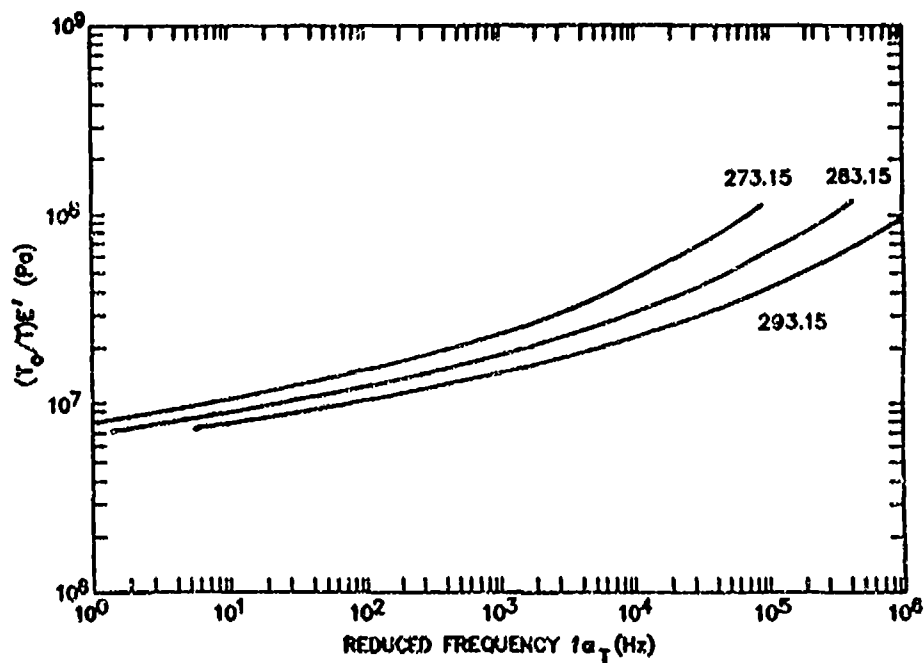


Fig. 8.5 - Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-5

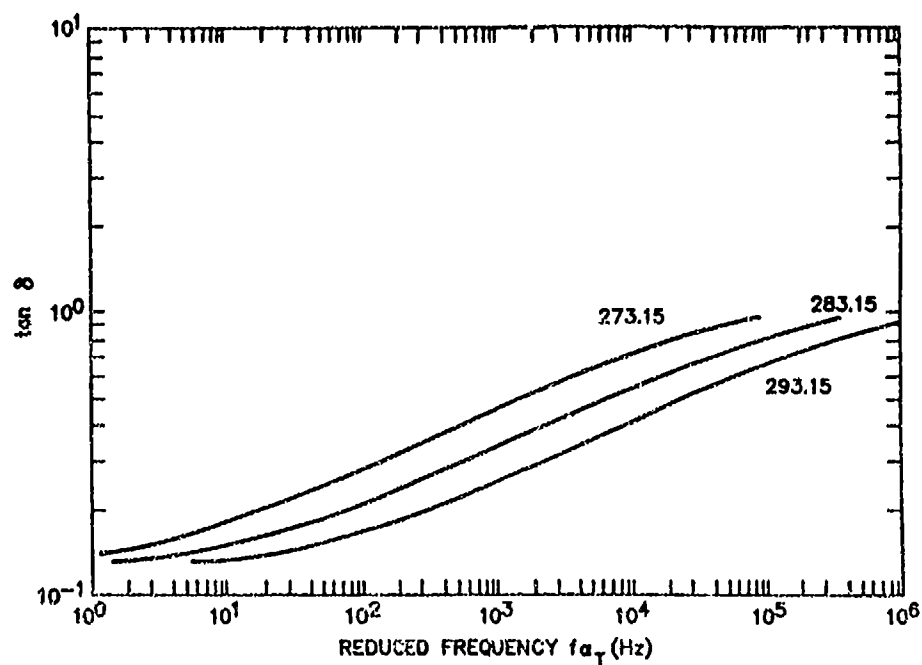


Fig. 8.6 - Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 165-6

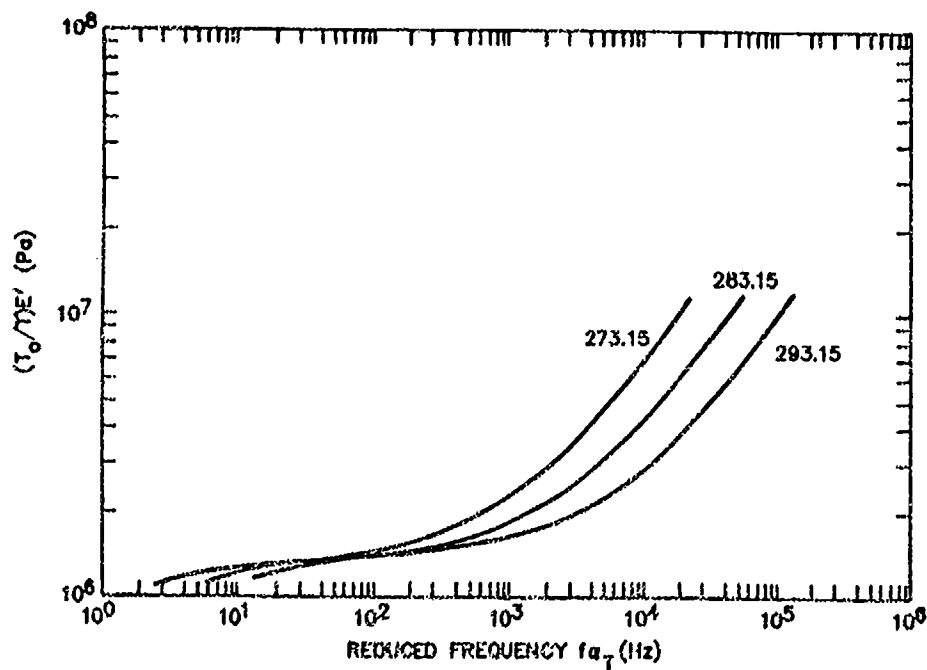


Fig. 8.7 - Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation 884-391

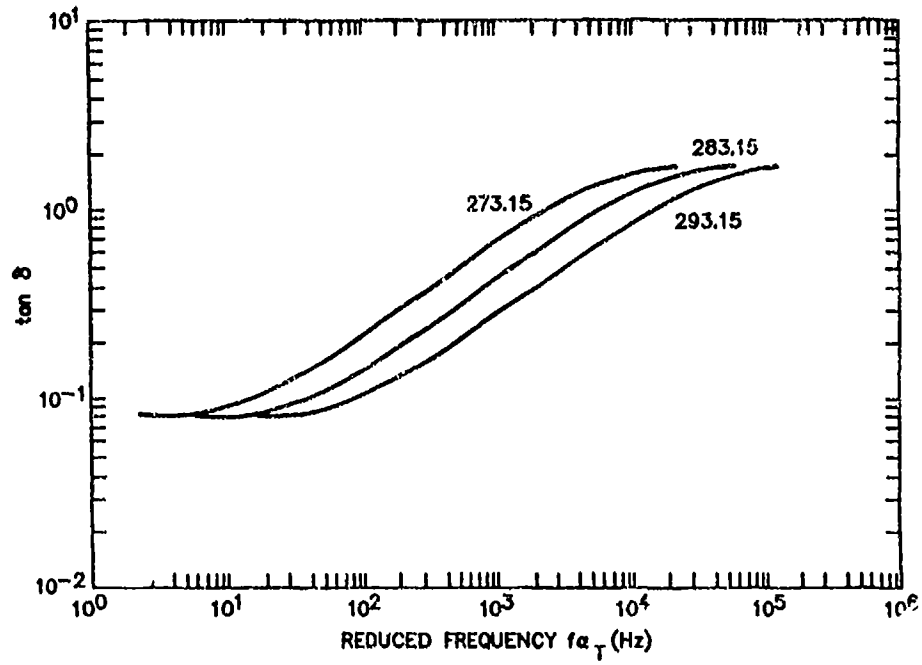


Fig. 8.8 - Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation 884-291

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CHAPTER 9

POLYCHLOROPRENE (NEOPRENE) RUBBERS (CR)

9.1 GENERAL INFORMATION

Neoprenes (ASTM D1418 designation CR) are a general class of elastomer (polychloroprene) obtained by the emulsion polymerization of 2-chloro-1,3-butadiene. This polymerization results in a molecular structure composed primarily of trans-chloro-2-butenylene units. However, some cis-1,4 addition, as well as 1,2 and 3,4 addition, occurs. The 1,2 addition results in the presence of allylic chlorine, which is believed to be the principal site for crosslinking^{327,334}.

Neoprene has been commercially available since 1931. Currently available types are classified as general-purpose, adhesive, or specialty. The general-purpose types are used in a variety of applications and comprise the class of neoprenes pertinent to underwater acoustic applications. There are various subclassifications within the general-purpose type, with differentiation based on the type of polymerization by which they were obtained^{327,334}. Types G and W are the two major subclassifications. Type W neoprenes have higher tensile properties and better storage stabilities than type G. Subtypes WRT and GRT contain comonomers for improved resistance to low-temperature crystallization and hardening, with WRT possessing the best crystallization resistance of any type of neoprene. The G type vulcanizates typically have better tear resistance, as well as being more flexible and resilient. Additionally, they are generally easier to bond to metals.

Vulcanization of neoprene formulations is dependent upon the presence of metallic oxides. Zinc oxide and magnesium oxide are typically used in a ratio of 4 to 5 phr of base polymer^{327,334,335}. The function of the magnesium oxide is believed to be to act as a chlorine scavenger. The use of metal oxides alone is sufficient to cure type G neoprenes. The cure rate with W types is impractically slow, so that organic accelerators such as ethylene thiourea must be used. Red lead (Pb_3O_4) or litharge (PbO) are frequently used in place of zinc and magnesium oxides when water resistance

and lower permeability are required^{335,336}. Other organic acceleration systems may be used in place of ethylene thiourea. A combination of sulfur and tetramethylthiuram monosulfide affords greater processing safety. Other systems that may be used include tetramethylthiuram monosulfide-sulfur-diorthotolylguanidine (DOTG) for compounds requiring a slow cure rate, salicylic acid for lightly loaded formulations where a high modulus is desired, and a combination of ethylene thiourea and the DOTG salt of dicatechol borate (Permalux) when a low-temperature cure rate is necessary^{327,334}.

An antioxidant is normally used in neoprene compounds, since unsaturation is present. At least 2 phr is normally incorporated, with more being added for increased heat and ozone resistance. P-phenylene diamines are a particularly effective class of antioxidant.

Both carbon blacks and mineral fillers are used extensively in neoprene compounds. Furnace carbon blacks offer good physical strength, while high-structure furnace blacks are good processing aids for extrusions and calendaring³²⁷. Addition of carbon blacks to neoprene causes less swelling upon exposure to water than did the corresponding gum stocks³³⁵. Use of conductive blacks causes the least amount of water swelling, followed by high- and medium-abrasion furnace blacks, thermal blacks, and the remaining furnace blacks^{335,336}. Mineral fillers generally cause more swelling than do the corresponding gum stocks. Hard clays and silica fillers (HI-SIL) are best for water resistance. Use of silica fillers has led to water blisters in underground cable applications³³⁵. Basic substances that react with hydrogen chloride, such as calcium carbonate, should not be used when compounding for water resistance.

Neoprenes as a class of elastomer have good resistance to weather, aging, and ozone. They will not support combustion. They have good abrasion and tear resistance. They are relatively impermeable to gases. Their electrical properties are not as intrinsically good as some other types of elastomers, such as butyl. They have good impact and flex resistance. Neoprenes possess fair resistance to oils, kerosene, and gasoline. They are resistant to acids and alkalis. They have poor resistance to benzene, halogenated solvents, and oxygenated solvents such

as low molecular weight esters and ethers. They have fair to good compatibility with hydraulic fluids containing both silicates and phosphates³¹¹.

9.2 SPECIFIC FORMULATIONS

Tables 9.1 and 9.2 give the basic formulations and typical physical properties for some neoprene GRT and WRT compounds, respectively, that were developed and evaluated for use in transducer applications at USRD^{337,338}. A variety of carbon blacks were evaluated in these systems¹⁰⁷. The viscoelastic properties of these materials were found to be strongly influenced by both the degree of loading and the particle size of the black used, as summarized in Figs. 3.4, 3.5, 3.6, 9.1, 9.2, and 9.3 and discussed in Chapter 3 in the section on fillers. Additionally, as shown in Tables 9.1 and 9.2, the tensile, tear and electrical properties of these materials were affected by both the type and degree of loading of black used. Varying the base polymer at equal loadings of the same black also gave differences in viscoelastic properties (Figs. 9.4 and 9.5 and Table 9.3). More complete discussions of the development of these formulations can be found in Refs. 337 and 338.

Some additional neoprene formulations³³⁹ are given in Table 9.4. Their viscoelastic properties are depicted graphically in Figs. 9.6 through 9.8. The last two formulations in this table are similar to the neoprene GRT formulations presented earlier, with the exception of different carbon black loading and incorporation of plasticizer in one of the compounds. As expected, the modulus increases and the loss tangent decreases as the amount of thermal black is increased.

TABLE 9.1 - FORMULATIONS AND PHYSICAL PROPERTIES OF NEOPRENE GRT
WITH 30-PHR LOADING OF DIFFERENT CARBON BLACKS

1858 SERIES:	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
COMPONENT	PHR					
Neoprene GRT	100.0	100.0	100.0	100.0	100.0	100.0
PEF N550	30.0					
N660		30.0				
SRF 774			30.0			
SL 90				30.0		
MT Black N990					30.0	
N539						30.0
Red Lead						
Polymer TRD 90	15.0	15.0	15.0	15.0	15.0	15.0
Octamine	2.0	2.0	2.0	2.0	2.0	2.0
Altax	1.5	1.5	1.5	1.5	1.5	1.5
Stearic Acid	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
Total pts by wt. =	149.5	149.5	149.5	149.5	149.5	149.5

STATIC PHYSICAL PROPERTIES:

PARAMETERS	VALUE						UNITS
Shore A Hardness	52	50	50	47	41	53	
Tens. Strength	18.0	17.1	20.3	16.0	9.71	25.8	MPa
Ult. Elongation	685	7705	715	750	660	690	%
300% Modulus	6.43	5.31	6.39	4.37	2.10	9.68	MPa
Sound Speed (1.8 MHz, 25°C)	1551	1548	1545	1543	1538	1551	m/s
Density	1420.7	1421.2	1417.4	1421.0	1423.3	1417.8	kg/m ³
Vol.Res. (10 ¹²)	1.3	1.1	1.4	1.1	0.79	1.2	ohm.cm
Cure Temperature	155	155	155	155	155	155	°C
Cure Time	45	45	45	45	45	45	min.

TABLE 9.2 - POLYNOMIAL COEFFICIENTS AND SHIFT CONSTANTS FOR
NEOPRENE GRT COMPOUNDS WITH 30-PHR LOADING OF DIFFERENT BLACKS

$\text{Log } a_T = \text{Shift Constant}(1/T - 1/T_0)$

$\text{Log } (E', \tan \delta) = \sum a_n [\log \text{freq (Hz)}]^n$

	<u>1858-5</u>	<u>1858-6</u>	<u>1858-7</u>	<u>1858-8</u>	<u>1858-9</u>	<u>1858-10</u>
<u>Modulus (283.15K)</u>						
a_0	6.8302	6.5754	6.7261	6.4573	6.387567	6.9654
a_1	0.11541	0.45576	0.16835	0.54600	0.336107	-0.23890
a_2	-0.028793	-0.31844	-0.10056	-0.40171	-0.19140	0.220237
a_3	0.010401	0.11181	0.044368	0.14051	0.0642553	-0.043084
a_4	-0.0013428	-0.010408	-0.0034965	-0.013860	-0.0047402	0.005029
<u>Tan δ (283.15K)</u>						
a_0	-0.85016	-1.1473	-1.0046	-1.1490	-1.1172	-1.1036
a_1	0.19794	0.37163	0.29980	0.44367	0.32361	0.34481
a_2	0.042056	0.013517	0.024836	-0.025857	0.043611	0.021022
a_3	-0.0087384	-0.007758	-0.008347	-0.0016838	-0.01184	-0.0089499
<u>Shift Constants</u>						
	6117	4650	5220	4829	4786	5031

Elastomeric Materials for Acoustical Applications

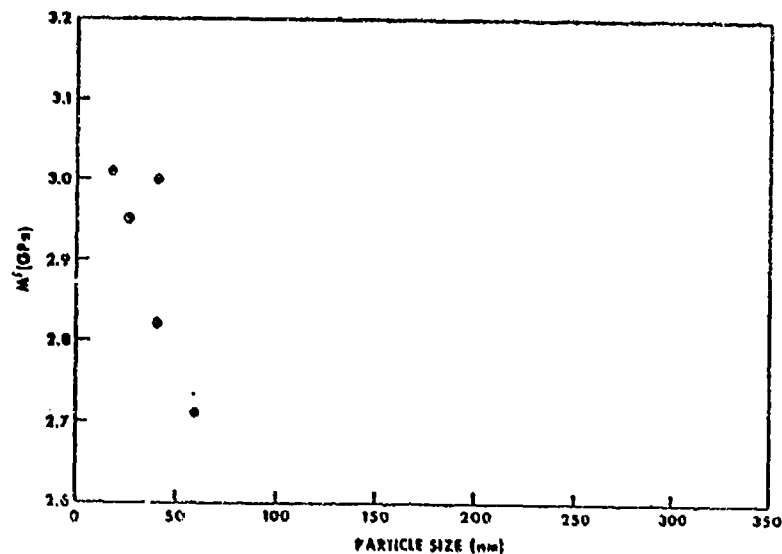


Fig. 9.1 - Plot of longitudinal storage modulus vs carbon black particle size for Neoprene CRT formulations with 35 phr loading at 295.65K and 3.15 MPa over the 4-kHz through 10-kHz range

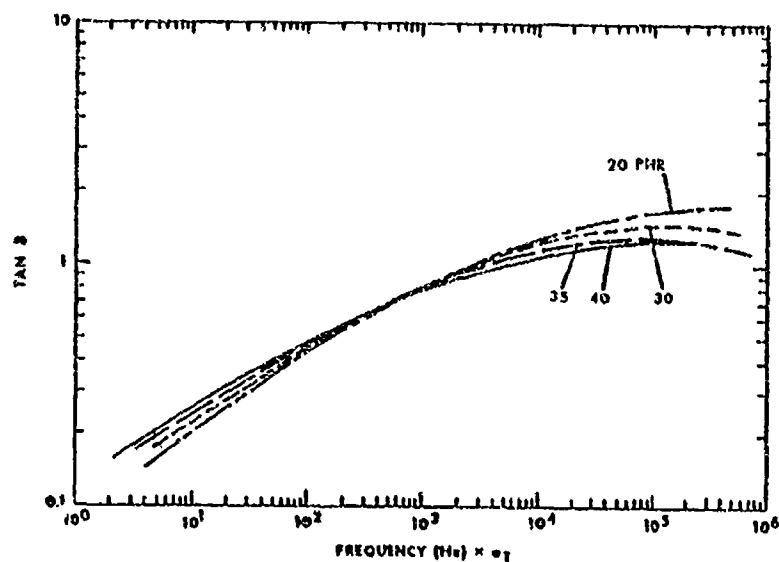


Fig. 9.2 - Plot of loss tangent vs reduced frequency for Neoprene CRT at 283.15K with various loadings of N660 black

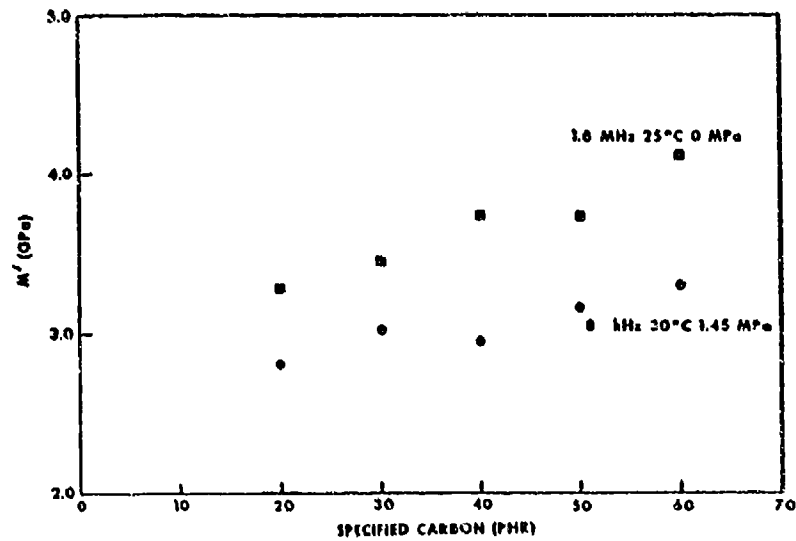


Fig. 9.3 - Effect of increased carbon black loading on longitudinal storage modulus for Neoprene WRT reinforced with N600 black

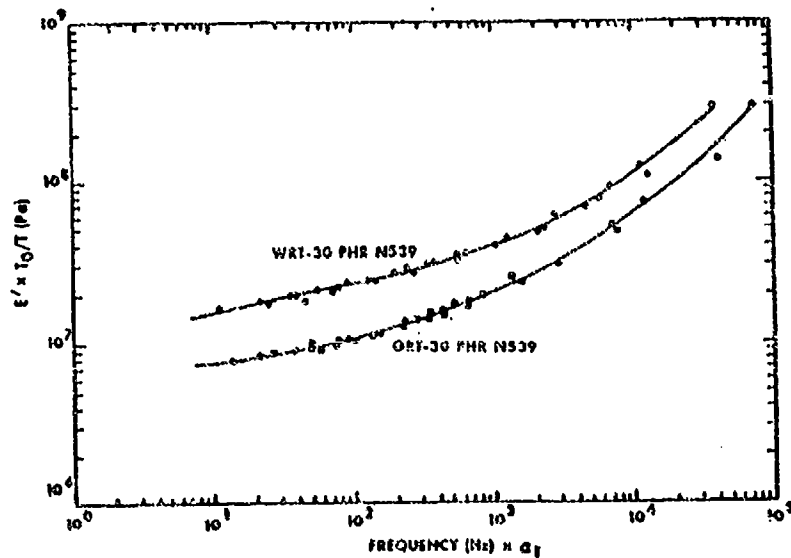


Fig. 9.4 - Comparison of storage Young's modulus vs reduced frequency at 288.15K for Neoprene GRT and WRT formulations reinforced with 80 phr FEF 530 black

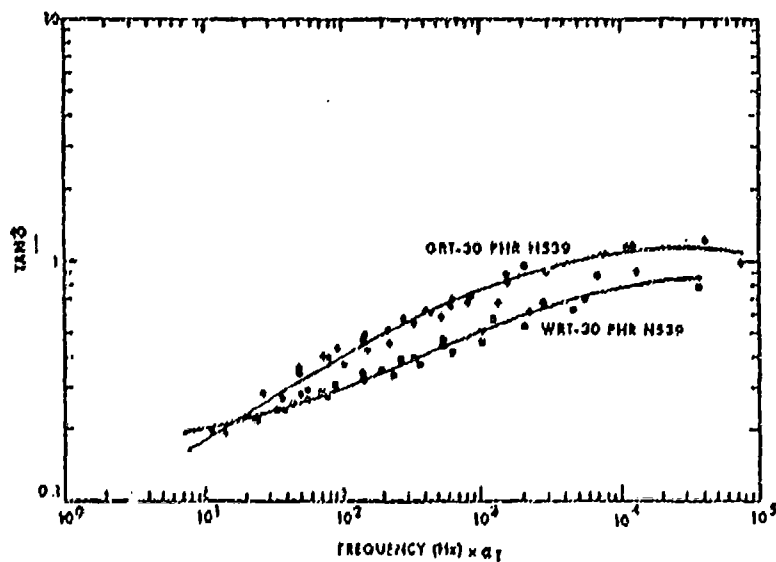


Fig. 9.5 - Comparison of loss tangent vs reduced frequency at 288.15K for Neoprene GRT and WRT formulations reinforced with 30 phr PBF 500 black

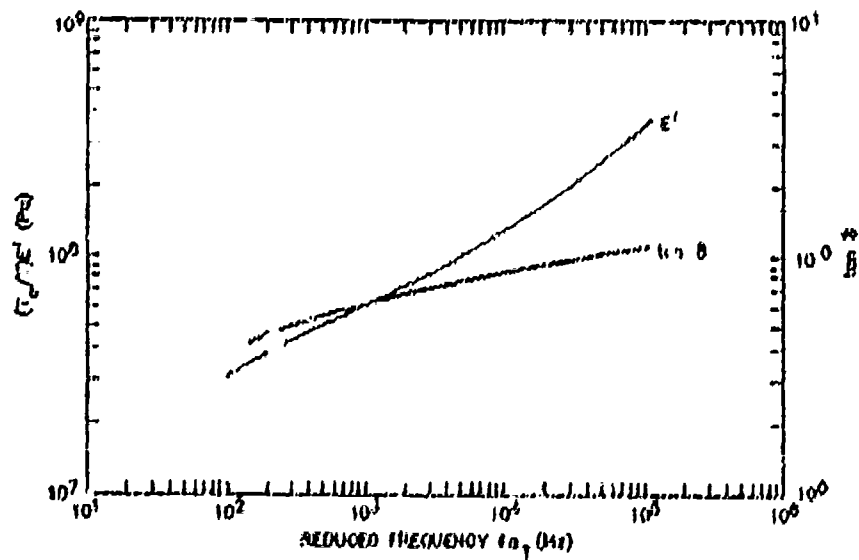


Fig. 9.6 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) at 288.15K for Buna S112 black

**TABLE 9.3 - FORMULATIONS AND PHYSICAL PROPERTIES OF NEOPRENE WRT COMPOUNDS
WITH VARYING LOADINGS OF N660 BLACK**

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>			
Neoprene WRT	100.0	100.0	100.0	100.0
N660 Black	20.0	30.0	35.0	40.0
Red Lead TRD90	15.0	15.0	15.0	15.0
Octamine	2.0	2.0	2.0	2.0
Thionex	2.0	2.0	2.0	2.0
Stearic Acid	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>
Total pts by wt =	139.5	149.5	154.5	159.5

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>				<u>UNITS</u>
Shore A Hardness	41	47	50	52	
Tensile Strength	20.3	19.6	19.0	19.5	MPa
Ultimate Elongtn.	731	544	520	470	%
300% Modulus	4.89	9.18	9.87	11.9	MPa
Sound Speed (1.8 MHz, 25°C)	1517	1546	1564	1599	m/s
Density	1424.1	1443.8	1458.6	1462.6	kg/m ³
Volume	1.14	1.17	0.40	0.92	10 ¹² ohm·cm
Cure Temperature	155	155	155	155	°C
90% Cure Time	45	45	45	45	min.

TABLE 9.4 - FORMULATIONS FOR ADDITIONAL NEOPRENE COMPOUNDS

<u>Ingredients</u>	<u>PHR</u>	
	<u>Burke</u> <u>5112</u>	<u>334-292</u>
Neoprene TRT	100.0	--
Neoprene GRT	--	100.0
Stearic Acid	0.3	1.0
Thermax (MT Black)	--	20.0
Philblack N550	40	20
Altax	0.35	1.5
Sulfur	0.5	--
Prespersion B1631		
(Red Lead)	15.0	15.0
Octamine	1.0	2.0
Thiurax	<u>1.0</u>	<u>--</u>
Total parts by weight =	158.15	159.5
<u>Press Cure</u>	30/160	20/160
(min. at °C)		
<u>Density (kg/m³)</u>	1460	1450
<u>Modulus (283.15K)</u>		
a_0	5.44555	6.76606
a_1	2.1369	0.11804
a_2	-0.81743	-0.026407
a_3	0.15103	0.017334
a_4	-0.0096518	-0.00071725
<u>Tan δ (283.15K)</u>		
a_0	-1.14230	-0.86518
a_1	0.62741	0.18097
a_2	-0.0900067	0.062306
a_3	0.0064144	-0.011858
$\text{Log } a_T =$	<u>-8.85 (T-283.15)</u>	5538 (1/T - 1/T ₀)
	117 + T - 283.15	

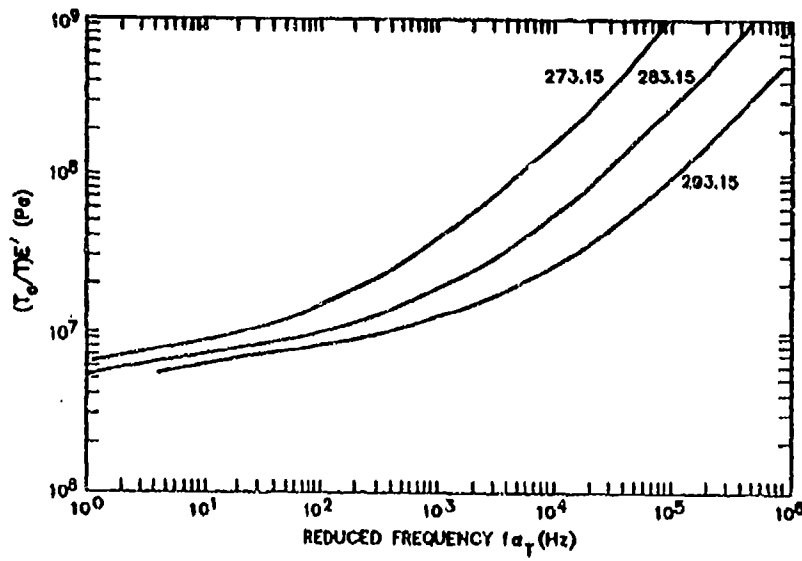


Fig. 9.7 - Plot of storage Young's modulus vs reduced frequency at three reference temperatures for DTNSRDC Neoprene 884-292

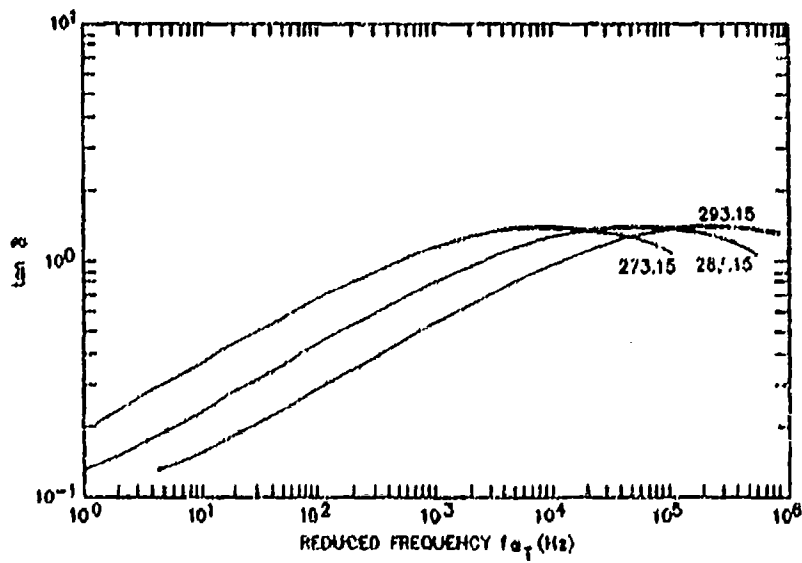


Fig. 9.8 - Plot of loss tangent vs reduced frequency at three reference temperatures for DTNSRDC Neoprene 884-292

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CHAPTER 10

NITRILE RUBBERS (NBR)

10.1 GENERAL INFORMATION

Nitrile rubber is a copolymer of acrylonitrile (ACN) and butadiene. This class of material is also known by the other generic names of Buna N and NBR. The monomer ratio of butadiene to ACN can be varied over a wide range to give materials with varying percentages of ACN content. Commercially available materials have an ACN content ranging from approximately 20 to 50%. A discussion of the polymerization of nitrile rubbers can be found in Refs. 340 and 341.

The basic copolymer system can be modified by the addition of other monomers. These are normally acrylic, methacrylic, or itaconic acids to obtain specific end properties. The composition of the polymer will have a marked effect on the final properties of the vulcanizates. The ACN content of the polymer will have the greatest effect on the properties of the cured elastomer. Shore A hardness will typically increase with increasing ACN content, along with compression set. Increasing the ACN content will cause the tensile strength to increase up to an ACN content of approximately 40%, after which it decreases³⁴². Increasing the ACN content will also increase the low temperature brittleness point.

Nitrile rubbers are amorphous polymers, so that pure gum vulcanizates have poor stress-strain properties. Use of carbon black or reinforcing mineral fillers is necessary to obtain optimum tensile properties. The resilience of nitrile rubber is lower than that of NR, CR, or SBR, but higher than that of IIR. The resilience of the rubber increases as the ACN content decreases. Nitrile rubbers are not normally used where heat build up on flexure is a potential problem.

Nitrile rubbers are vulcanized by essentially the same cure systems as SBR or NR. Proportions of ingredients may vary somewhat from those used with NR. Sulfur/accelerator, sulfur donor, or peroxide cures may be used³⁴². The cure curve is relatively flat; therefore small variations in

amounts of curatives or time and temperature do not lead to serious problems in the vulcanizate³⁴². Optimization of the cure is generally measured by the tensile modulus. Carboxylic nitrile polymers are cured in a similar manner, but require the use of special grades of zinc oxide.

Nitrile rubbers do not possess electrical properties that render them suitable for use as primary insulators. Instead, they can be compounded to give conductive elastomers. If insulation use is a priority, mineral fillers and the best water-resistant types of polymers should be used.

Permeability of nitrile rubbers to gases is essentially the same as that of butyl rubbers. Increasing the ACN content increases the permeation resistance³⁴².

One of the outstanding characteristics of nitrile rubbers is their resistance to petroleum oils and gasoline. They also have good resistance to aromatic hydrocarbons such as benzene and toluene³⁴³. Nitrile rubber also has excellent resistance to mineral and vegetable oils, but tends to undergo severe swelling in the presence of oxygenated solvents such as acetone and methyl ethyl ketone. It also has generally poor resistance to halogenated solvents and hydraulic fluids. Increased ACN content tends to increase the solvent resistance at the expense of low-temperature flexibility.

Nitrile rubber has only fair resistance to aging and ozone; therefore use of antioxidants is required for good environmental resistance. Nitrile rubber has good abrasion, tear, and impact resistance. Its creep-resistant and stress-relaxation properties are also good.

Nitrile rubbers can be blended with a variety of other types of polymers, such as vinyl chloride, phenolic and ABS resins, SBR, CR, chlorosulfonated polyethylene, and NR to a certain extent. These are used to impart variations in processing properties, oil and heat resistance, low temperature flexibility, or cost. A common cure system can generally be used for both types of polymers in the blend.

10.2 SPECIFIC FORMULATIONS

Nitrile rubber formulations have been used for underwater acoustic applications. Studies dealing with NBR have been conducted by several investigators. Cramer and Silver²⁵⁵ examined particle-size effects of different carbon blacks on NBR formulations. Cook, Lee, and Fitzgerald²⁵⁶ examined NBR formulations with both varying percentages of bound ACN content and varying carbon black content. They also measured the effects on viscoelastic properties due to a limited number of different types of carbon black. Their results indicated that the shear storage compliance, J' , tended to decrease with increasing frequency at 25°C as a function of increasing ACN content (equivalent to an increase in the shear storage modulus, G'). The loss tangent tended to increase. The storage compliance also decreased with increased loading of carbon black, while the effect on the loss tangent varied depending upon the temperature of measurement.

Lee, Madigosky, and Eynck⁷⁵ evaluated a number of NBR formulations with different cure systems and different types and loadings of fillers. Some of these are included here.

Master frequency curves⁷⁵ at a reference temperature of 10°C for the nitrile formulations in Table 10.1 are shown in Figs. 10.1 and 10.2. These are red lead, sulfur-cured NBR formulations with an ACN content of 38% (Paracril CLT). The carbon black content is varied in this formulation for two different types of carbon black. It can be seen that increasing the carbon black loading increases the storage modulus, while causing a decrease in the loss tangent. The N550 black also causes a greater degree of reinforcement than Thermax.

The same formulation with a lower loading of N550 carbon black and two different loadings of iron oxide filler (Table 10.2) is shown in Figs. 10.3 and 10.4. In contrast to the carbon black, the net effect of the iron appears to be primarily one of mechanical reinforcement, causing the same rate of change in both the storage and loss moduli. The net effect is that the storage modulus increases as the iron oxide loading increases, but the iron oxide does not cause a change in the loss tangent.

TABLE 10.1 - NSWC PARACRIL CLT FORMULATIONS

314 SERIES:	<u>818</u>	<u>1057</u>	<u>1058</u>	<u>1059</u>	
<u>COMPONENT</u>	<u>PHR</u>				
Paracril CLT	100.0	100.0	100.0	100.0	
Philblack N-550	50.0	70.0			
Thermax			80.0	120.0	
Fyrol CEF	5.0	5.0	5.0	5.0	
Protox 166	5.0	5.0	5.0	5.0	
Sulfur	1.5	1.5	1.5	1.5	
Octamine	1.0	1.0	1.0	1.0	
Stearic Acid	1.0	1.0	1.0	1.0	
Thionex	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	<u>0.5</u>	
Total pts by wt. =	164.0	184.0	194.0	234.0	
STATIC PHYSICAL PROPERTIES:					
<u>PARAMETERS</u>	<u>VALUE</u>				<u>UNITS</u>
Density	1224.4	1267.8	1291.0	1367.5	kg/m ³
Cure Temperature	160	160	160	160	°C
90% Cure Time	25	25	25	25	min.
SHIFT PARAMETERS: $\text{Log } a_T = -c_1 (T - 283.15) / (c_2 + T - 283.15)$					
c_1	5.48	8.71	19.0	4.2	
c_2	56	106	220	46	
<u>Modulus (283.15K)</u>					
a_0	7.72582	7.95059	7.94078	8.29487	
a_1	-0.27037	-0.52918	-1.06015	-0.97612	
a_2	0.063436	0.31848	0.59403	0.47402	
a_3	0.046803	-0.029902	-0.093571	-0.055530	
a_4	-0.007278	-0.00021301	0.0058107	0.0016107	
<u>Tan δ (283.15K)</u>					
a_0	-1.3555	-0.61512	-0.96763	-1.44560	
a_1	0.99088	0.40390	0.77414	0.97342	
a_2	-0.19145	-0.047726	-0.13668	-0.16722	
a_3	0.0063779	-0.0048541	0.0012512	0.0035766	

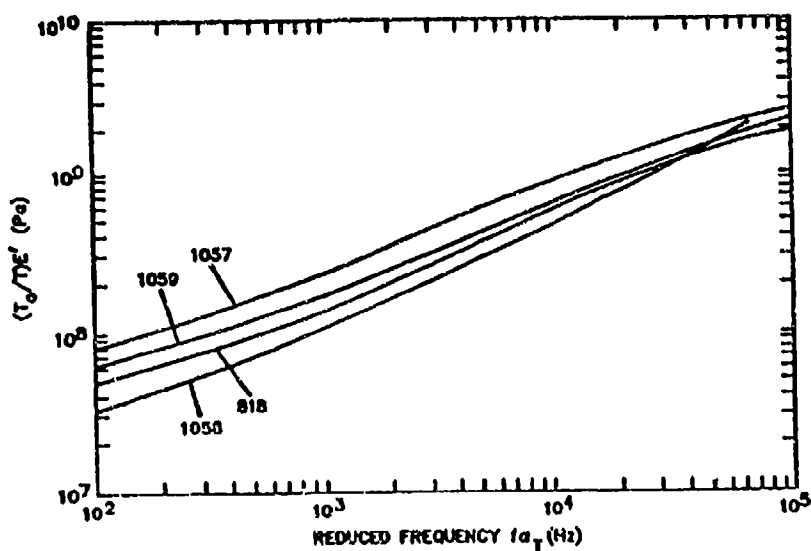


Fig. 10.1 - Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with different loadings of N550 black

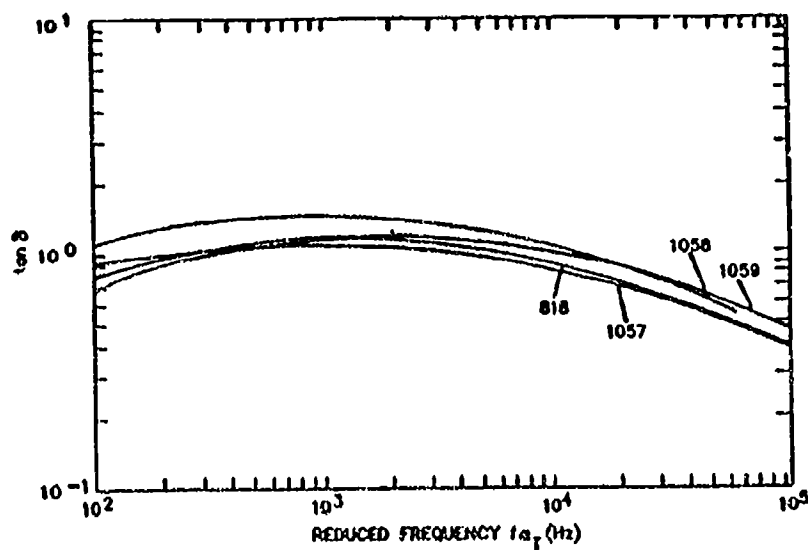


Fig. 10.2 - Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with different loadings of N550 black

TABLE 10.2 - NSWC PARACRIL CLT FORMULATIONS WITH IRON OXIDE FILLER

314 SERIES:	<u>1060</u>	<u>1061</u>
<u>COMPONENT</u>	<u>PHR</u>	
Paracril CLT	100.0	100.0
Iron Oxide	100.0	200.0
Philblack N-550	20.0	20.0
Fyrol CEF	5.0	5.0
Protox 166	5.0	5.0
Sulfur	1.5	1.5
Octamine	1.0	1.0
Stearic Acid	1.0	1.0
Thionex	<u>0.5</u>	<u>0.5</u>
Total parts by weight =	234.0	334.0

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1692.3	kg/m ³
Cure Temperature	160	°C
90% Cure Time	25	min.

SHIFT PARAMETERS: $\log a_T = -c_1 (T - 283.15) / (c_2 + T - 283.15)$

c_1	7.76	81.0
c_2	2.84	30.0

Modulus (283.15K)

a_0	7.4430	9.4197
a_1	0.28040	-2.1886
a_2	-0.21081	1.0236
a_3	0.099002	-0.15430
a_4	-0.010622	-0.0075550

Tan δ (283.15K)

a_0	-1.1297	0.64925
a_1	0.72108	-0.61998
a_2	-0.090698	0.22016
a_3	-0.0050144	-0.027454

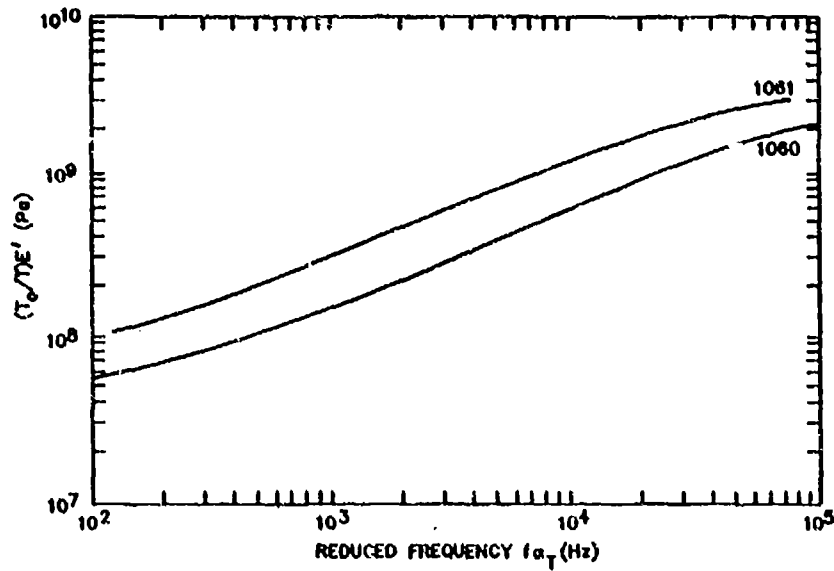


Fig. 18.3 - Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of iron oxide filler

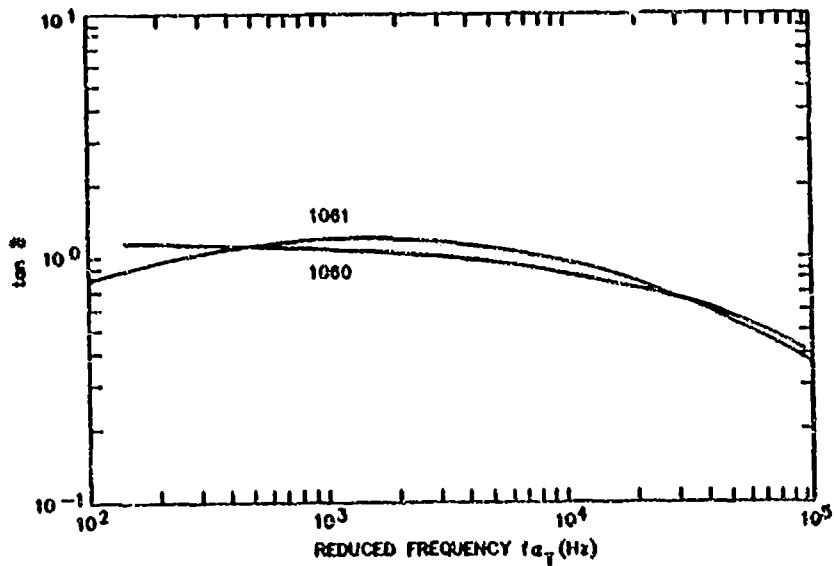


Fig. 18.4 - Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of iron oxide filler

Silane-treated silica was also investigated as a filler in this rubber system. The formulations are given in Table 10.3, with the master curves shown in Figs. 10.5 and 10.6. Increasing the loading of silica increases the modulus but has little effect on the loss tangent. A comparison of the effects of the carbon black and the silica at equal loading is shown by comparing the master curves for formulations 314-818 and 314-1063. The carbon black causes an increase in the storage modulus relative to the silica but the loss tangent is decreased.

Peroxide cure systems were also used with the Paracril CLT. The formulations listed in Table 10.4 contain varying proportions of Saret 500, which is an acrylic crosslinking agent that is used as a curing coagent with dicumyl peroxide. Master curves for these formulations are shown in Figs. 10.7 and 10.8. It can be seen that increasing the concentration of curing coagent causes an increase in the storage modulus at low frequencies, with little effect at higher frequencies. This can be taken as evidence that the degree of crosslinking in the formulation is increasing with increasing concentration of coagent^{229,344}. Use of excess coagent (formulation 314-1067) had little effect. Use of a different coagent (Saret 515, Table 10.5) gave vulcanizates with a higher modulus and lower loss tangent (Figs. 10.9 and 10.10).

A number of different types of fillers at equal loadings were evaluated in the same elastomer system to determine their relative effects on the modulus and loss tangent (Table 10.6). The effect observed upon the modulus was that carbon black gave a greater degree of reinforcement than did either hydrated silica or silane-treated silica, both of which were more reinforcing than was titanium dioxide (cf. Fig. 10.11). The effects on the loss tangent were not as clear cut (Fig. 10.12). This can be attributed primarily to the differences in the degree of chemical interaction between the rubber matrix and the various fillers, with resultant differences in degree of aggregation and distribution of stress when the rubber material is subjected to a frequency-dependent excitation.

TABLE 10.3 - NSWC PARACRIL CLT FORMULATIONS WITH SILICA FILLER

314 SERIES:	<u>1062</u>	<u>1063</u>
<u>COMPONENT</u>	<u>PHR</u>	
Paracril CLT	100.0	100.0
QUSO WR 82	30.0	50.0
Fyrol CEF	5.0	5.0
Protox 166	5.0	5.0
Sulfur	1.5	1.5
Octamine	1.0	1.0
Stearic Acid	1.0	1.0
Thionex	<u>0.5</u>	<u>0.5</u>
Total parts by weight =	144.0	164.0

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>		<u>UNITS</u>
Density	1177.1	1235.0	kg/m ³
Cure Temperature	160	160	°C
90% Cure Time	25	25	min.

SHIFT PARAMETERS: $\text{Log } a_T = -c_1(T - 283.15)/(c_2 + T - 283.15)$

c_1	4.6	7.18
c_2	45	93

Modulus (283.15K)

a_0	4.051057	8.7406
a_1	3.75296	-1.7348
a_2	-1.6486	0.82357
a_3	0.35681	-0.12601
a_4	-0.027532	0.0068266

Tan δ (283.15K)

a_0	-1.7883	-1.8453
a_1	1.4600	1.2657
a_2	-0.32724	-0.23450
a_3	0.019533	0.0086048

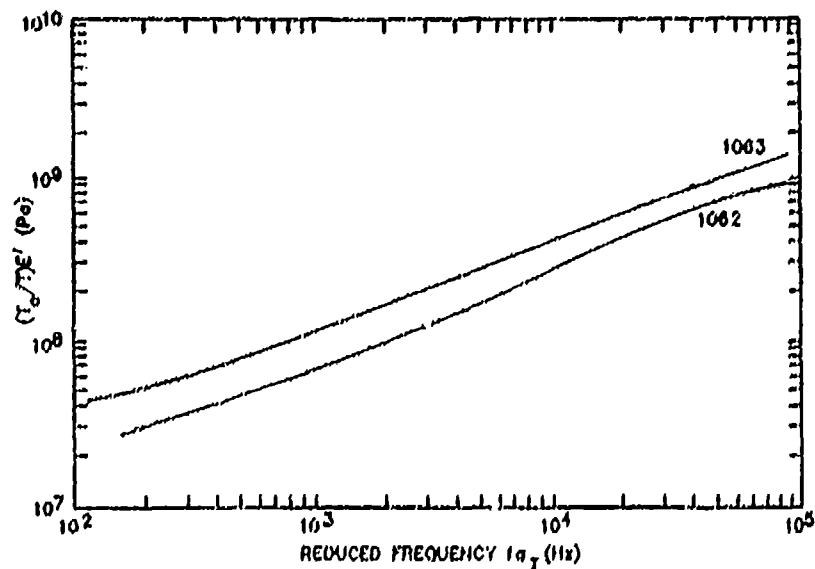


Fig. 10.8 - Plot of storage Young's modulus vs reduced frequency at 288.15K for Paracril OLT formulations with two different loadings of silica filler

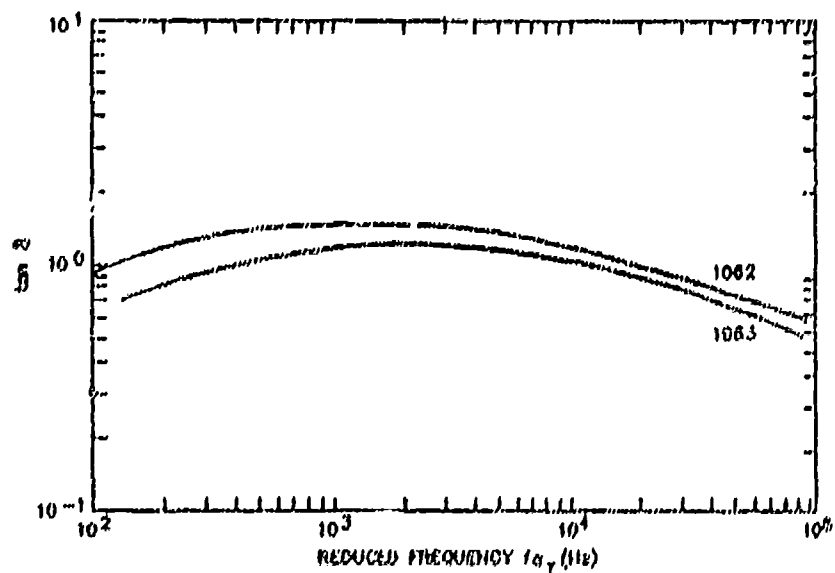


Fig. 10.9 - Plot of loss tangent vs reduced frequency at 288.15K for Paracril OLT formulations with two different loadings of silica filler

TABLE 10.4 - NSWC NITRILE FORMULATIONS WITH SARET 500 PEROXIDE CURE

314 SERIES:	<u>1064</u>	<u>1065</u>	<u>1066</u>	<u>1067</u>	
<u>COMPONENT</u>	<u>PHR</u>				
Paracril CLT	100.0	100.0	100.0	100.0	
Philblack N-550	50.0	50.0	50.0	50.0	
Protox 166	5.0	5.0	5.0	5.0	
Saret 500	0.0	5.0	10.0	20.0	
DiCUP 40 Peroxide	4.0	4.0	4.0	4.0	
Octamine	<u>2.0</u>	<u>2.0</u>	<u>2.0</u>	<u>2.0</u>	
Total pts by wt. =	161.0	166.0	171.0	181.0	
STATIC PHYSICAL:					
<u>PARAMETERS</u>	<u>VALUE</u>				<u>UNITS</u>
Density	1219.7	1221.5	1219.9	1222.4	kg/m ³
Cure Temperature	160	160	160	160	°C
90% Cure Time	25	25	25	25	min.
SHIFT PARAMETERS: $\text{Log } a_T = -c_1 (T - 283.15)/(c_2 + T - 283.15)$					
c_1	6.3	10.6	7.5	4.42	
c_2	93.0	129	74.0	46.0	
<u>Modulus (283.15K)</u>					
a_0	7.7431	7.47082	8.2092	6.8258	
a_1	-0.21846	-0.049916	-0.76348	0.85701	
a_2	-0.023592	0.15708	0.46360	-0.15318	
a_3	0.069918	-0.012843	-0.068009	0.028610	
a_4	-0.0087952	-0.00028422	0.0029654	-0.0024520	
<u>Tan δ (283.15K)</u>					
a_0	-1.1926	0.38204	-0.86980	-0.95216	
a_1	0.72233	-0.39474	0.63540	0.75772	
a_2	-0.076964	0.18095	-0.12462	-0.19678	
a_3	-0.0074113	-0.027137	0.0025469	0.013440	

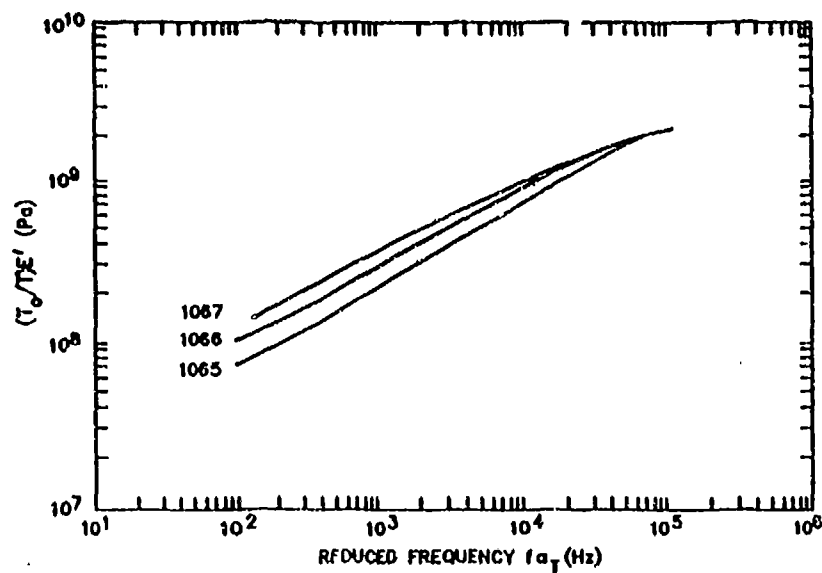


Fig. 15.7 - Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of peroxide curing coagent

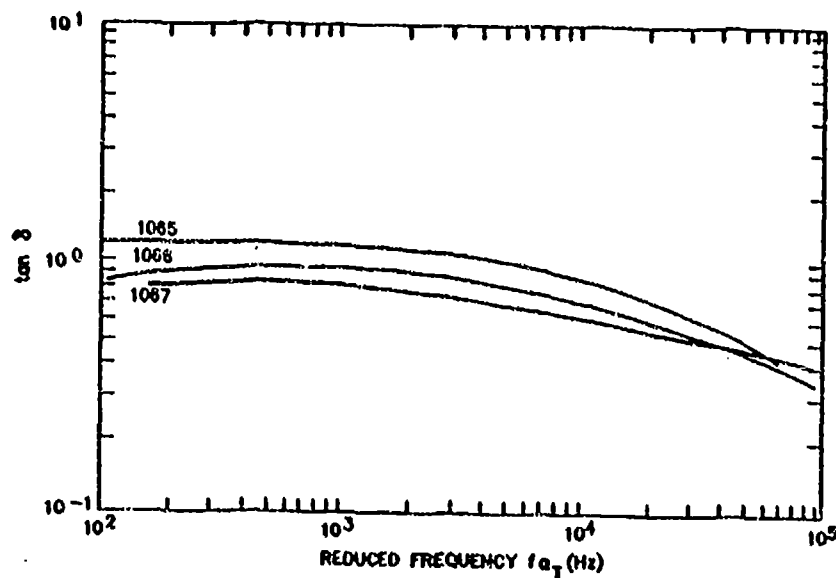


Fig. 15.8 - Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of peroxide curing agent

TABLE 10.5 - NSWC PARACRIL CLT FORMULATIONS
WITH SARET 515 PEROXIDE CURE

314 SERIES:	<u>1068</u>	<u>1069</u>	<u>1070</u>	
<u>COMPONENT</u>	<u>PHR</u>			
Paracril CLT	100.0	100.0	100.0	
Philblack N-550	50.0	50.0	50.0	
Protox 166	5.0	5.0	5.0	
Saret 515	5.0	10.0	20.0	
DiCUP 40 Peroxide	4.0	4.0	4.0	
Octamine	<u>2.0</u>	<u>2.0</u>	<u>2.0</u>	
Total parts by wt. =	166.0	171.0	181.0	
STATIC PHYSICAL PROPERTIES:				
<u>PARAMETERS</u>	<u>VALUE</u>			<u>UNITS</u>
Density	1220.3	1226.0	1222.0	kg/m ³
Cure Temperature	160	160	160	°C
90% Cure Time	25	25	25	min.
SHIFT PARAMETERS: $\text{Log } a_T = -c_1(T - 283.15) / (c_2 + T - 283.15)$				
c_1	10.3	15.5	12.0	
c_2	100	160	137	
<u>Modulus (283.15K)</u>				
a_0	9.1987	7.4808	7.2330	
a_1	-1.9357	0.45265	0.48120	
a_2	0.96965	-0.037037	0.015968	
a_3	-0.16013	0.011607	-0.0051293	
a_4	0.0088485	-0.0013783	-0.000042606	
<u>Tan δ (283.15K)</u>				
a_0	-1.5592	-0.82223	-0.12186	
a_1	1.2655	0.43118	0.14386	
a_2	-0.30830	-0.043627	-0.063280	
a_3	0.020019	-0.0059362	0.0043116	

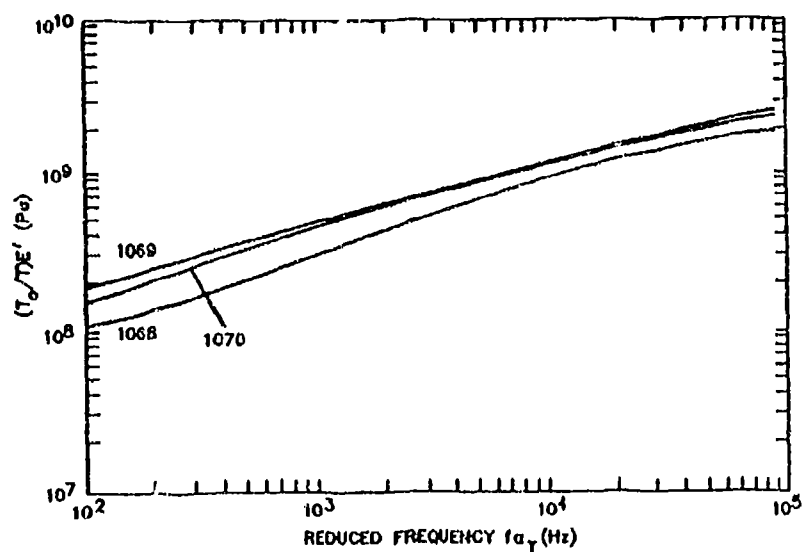


Fig. 10.9 - Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of different peroxide curing coagent

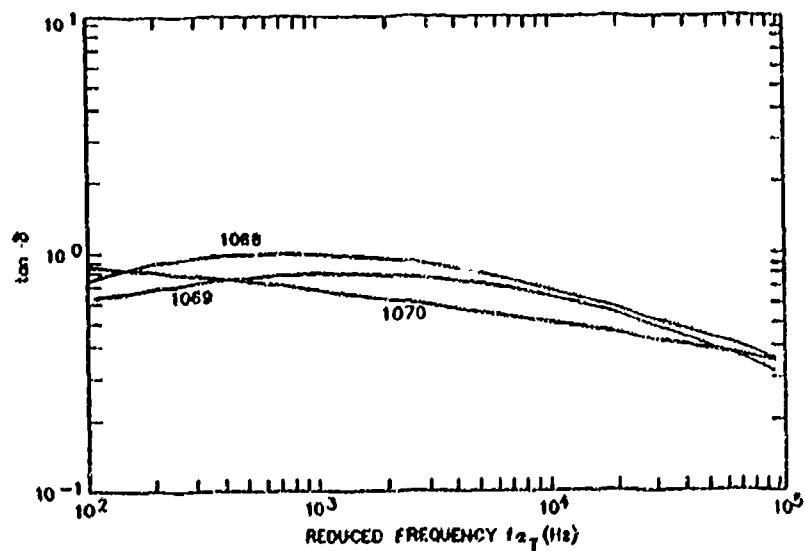


Fig. 10.10 - Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of different peroxide curing coagent

TABLE 10.6 - NSWC PARACRIL CLT FORMULATIONS
WITH PEROXYDIE CURE AND DIFFERENT FILLERS

1470 SERIES:	<u>1478</u>	<u>1479</u>	<u>1480</u>	<u>1481</u>	
<u>COMPONENT</u>	<u>(PHR)</u>				
Paracril GLT	100.0	100.0	100.0	100.0	
Protox 166	5.0	5.0	5.0	5.0	
Vul-CUP 40 KE	3.0	3.0	3.0	3.0	
Stearic Acid	1.0	1.0	1.0	1.0	
Age Rite Resin D	0.5	0.5	0.5	0.5	
Philblack N 440	40.0				
QUSO WR 82		40.0			
Hi-Sil 223			40.0		
TiO				<u>40.0</u>	
Total pts by wt. =	149.5	149.5	149.5	149.5	
STATIC PHYSICAL PROPERTIES:					
<u>PARAMETERS</u>	<u>VALUE</u>				<u>UNITS</u>
Density	1188.2	1207.8	1214.9	1305.7	kg/m ³
Cure Temperature	160	160	160	160	°C
Cure Time	25	25	25	25	min.
SHIFT PARAMETERS:	Log a _T = -c ₁ (T - 283.15) / (c ₂ + T - 283.15)				
c ₁	18.9	12.9	2.8	15.2	
c ₂	180	117	32	160	
<u>Modulus (283.15K)</u>					
a ₀	0.4344	0.3781	8.2143	7.6291	
a ₁	0.78061	1.1539	-0.88720	-0.56180	
a ₂	-0.30919	-0.49357	0.40192	0.26675	
a ₃	0.10698	0.13406	-0.031169	-0.0059840	
a ₄	-0.011001	-0.011771	-0.0012415	-0.0025145	
<u>Tan δ (283.15K)</u>					
a ₀	0.48199	-0.60013	-2.22366	-2.6970	
a ₁	-0.36766	0.30872	1.3651	2.3388	
a ₂	0.16341	0.020760	-0.22918	-0.56287	
a ₃	-0.025103	-0.014841	0.0055744	0.036511	

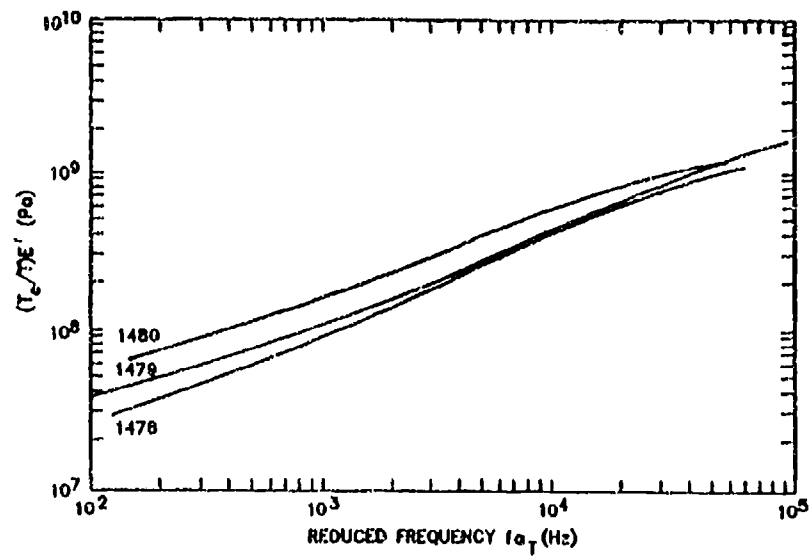


Fig. 18.11 - Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with varying peroxide cures and three different fillers

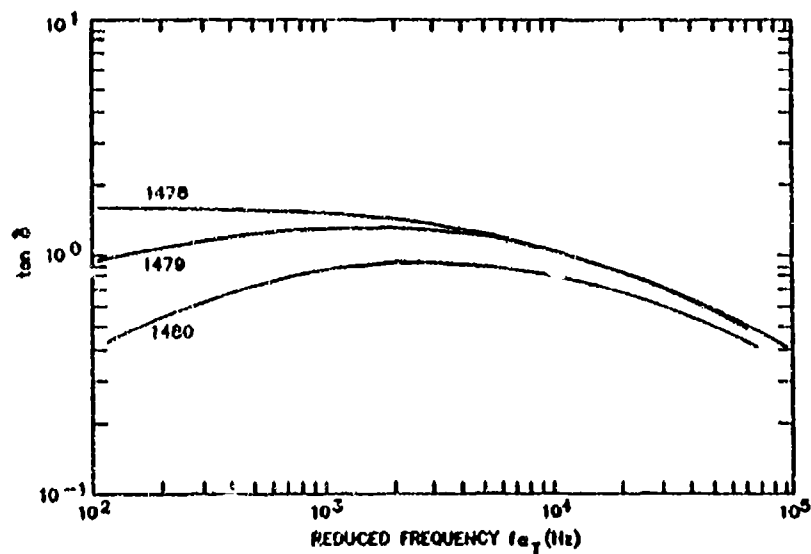


Fig. 18.12 - Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying peroxide cures and three different fillers

An extensive investigation of the effect of varying ACN content was not performed in this study. Thompson³⁴⁵ investigated several NBR formulations with different ACN content for use as vibration dampers in transducers (Table 10.7, Fig. 10.13, and Fig. 10.14). Over the range of ACN contents used (22 to 29.5%), increasing the ACN content causes a slight increase in the storage modulus at higher frequencies, an increase in the loss tangent, as well as a frequency shift in the location of the maximum of the loss tangent at a constant temperature. A more noticeable effect is observed for a formulation of given ACN content (Table 10.8 and Figs. 10.15 and 10.16) if the carbon black content is increased. The modulus tends to increase as a function of frequency, while the loss tangent decreases.

TABLE 10.7 - NBR FORMULATIONS WITH VARYING ACN CONTENT

FORMULATION:	256-3	255-1	
COMPONENT	PHR		
Paracril 18-8OLM	100.0		
Paracril BJ		100.0	
N550 Black	45.0	45.0	
Zinc Oxide	5.0	5.0	
Octamine	2.0	2.0	
Sulfur	1.5	1.5	
Stearic Acid	1.0	1.0	
TMTMS	0.5	0.5	
Total parts by weight =	155.0	155.0	
PARAMETERS	VALUE		UNITS
Density	1145	1148	kg/m ³
Cure Temp.	155	155	°C
Cure Time	18	9	min.
SHIFT PARAMETERS: $\text{Log } a_T = \text{Shift Constant } (1/T - 1/T_0)$			
Shift Constants	5904	6452	
<u>Modulus (283.15K)</u>			
a ₀	7.1028	7.0312	
a ₁	0.24492	0.22143	
a ₂	-0.11008	-0.14399	
a ₃	0.033942	0.06085	
a ₄	-0.0023231	-0.0054709	
<u>Tan delta (283.15K)</u>			
a ₀	-0.82360	-0.68485	
a ₁	0.088877	0.18215	
a ₂	0.065901	0.037680	
a ₃	-0.010309	-0.0097497	

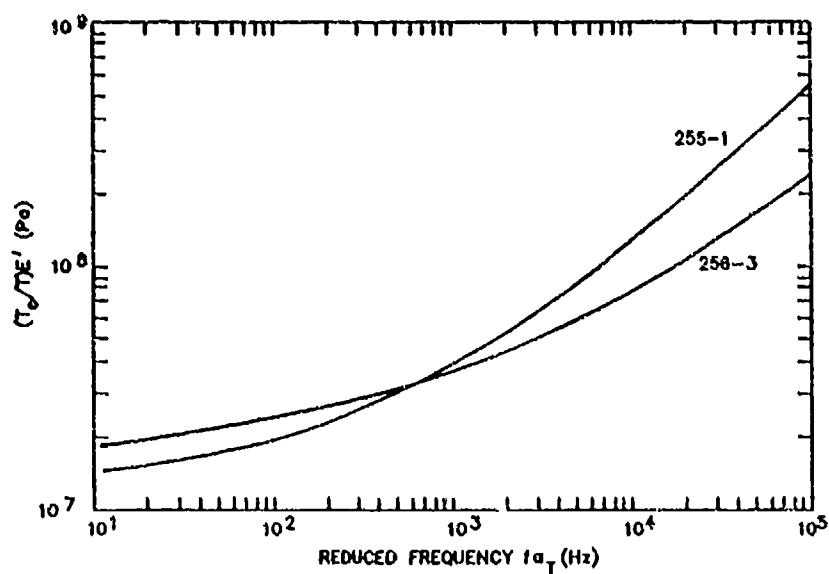


Fig. 10.13 - Plot of storage Young's modulus vs reduced frequency at 283.15K for nitrile formulations with varying ACN content

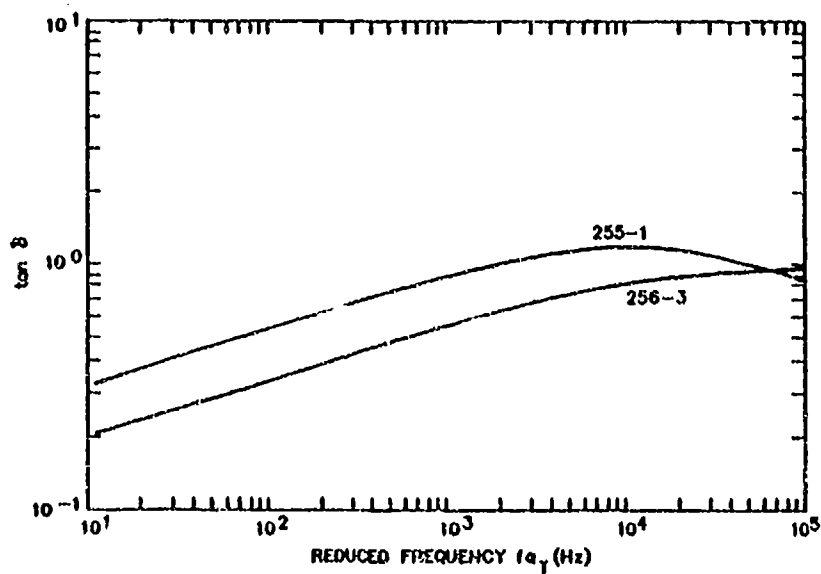


Fig. 10.14 - Plot of loss tangent vs reduced frequency at 283.15K for nitrile formulations with varying ACN content

TABLE 10.8 - NITRILE FORMULATIONS WITH 26% ACN CONTENT
AND VARYING LOADINGS OF CARBON BLACK

FORMULATION:	<u>257-2</u>	<u>257-3</u>	<u>257-4</u>	
<u>COMPONENT</u>				
Paracril ALT	100.0	100.0	100.0	
N550 Black	65.0	75.0	85.0	
Fyrol CEF	5.0	5.0	5.0	
Zinc Oxide	5.0	5.0	5.0	
Octamine	2.0	2.0	2.0	
Sulfur	1.5	1.5	1.5	
Stearic Acid	1.0	1.0	1.0	
TMTMS	0.5	0.5	0.5	
<hr/>				
Total pts by wt. =	180.0	190.0	200.0	
<u>PARAMETERS</u>	<u>VALUE</u>			<u>UNITS</u>
Density	1206	1229	1244	kg/m ³
Cure Temperature	155	155	155	°C
Cure Time	14	11	22	min.
 SHIFT PARAMETERS: $\text{Log } a_T = \text{Shift constant } (1/T - 1/T_0)$				
Shift Constants	6785	6835	7290	
 <u>Modulus (283.15K)</u>				
a_0	7.3336	7.5039	7.6344	
a_1	0.26660	0.18863	0.18791	
a_2	-0.12357	-0.075040	-0.058712	
a_3	0.037211	0.027552	0.018965	
a_4	-0.0026231	-0.0021038	-0.0012071	
 <u>Tan δ (283.15K)</u>				
a_0	-0.72609	-0.75340	-0.73483	
a_1	-0.0023684	0.052568	0.010778	
a_2	0.091878	0.068152	0.074009	
a_3	-0.013086	-0.010657	-0.010406	

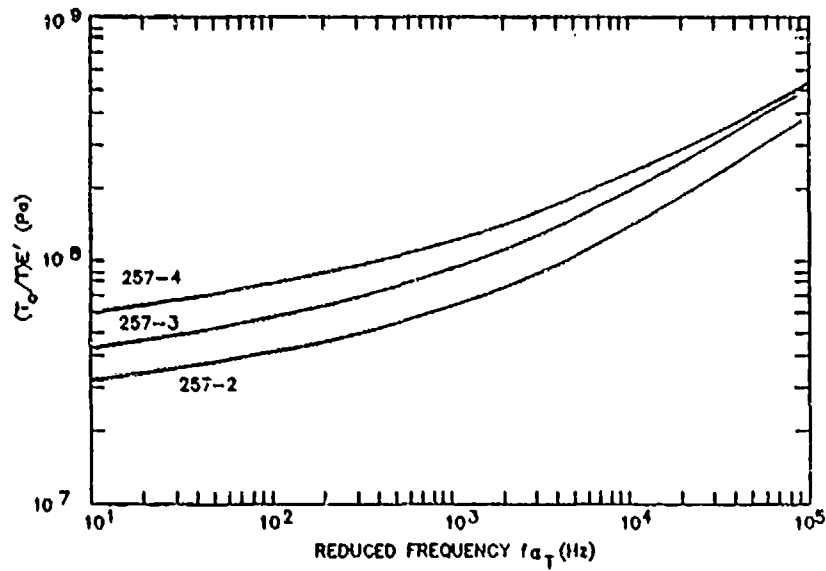


Fig. 10.15 - Plot of storage Young's modulus vs reduced frequency at 288.15K for 26% ACN formulations with varying amounts of N550 black

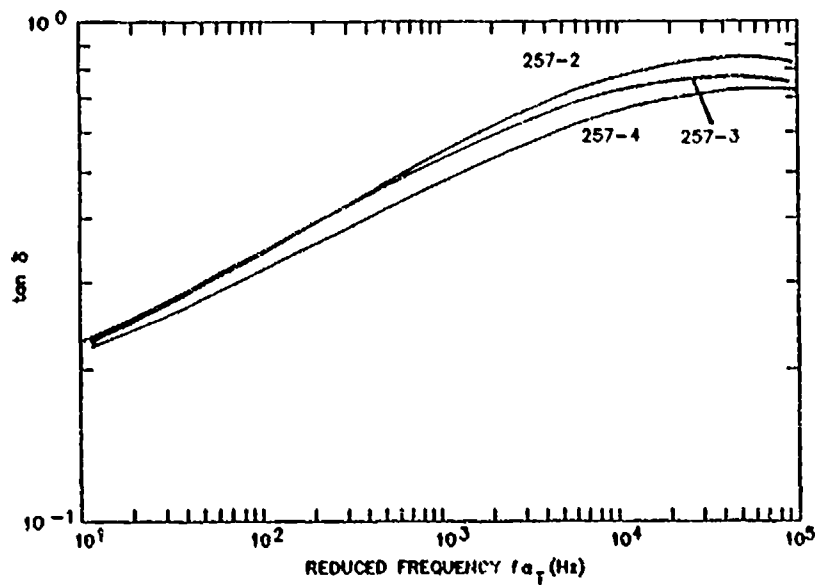


Fig. 10.16 - Plot of loss tangent vs reduced frequency at 288.15K for 26% ACN formulations with varying amounts of N550 black

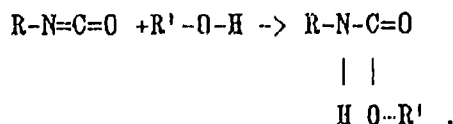
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CHAPTER 11

POLYURETHANES

11.1 GENERAL INFORMATION

Anyone whose college career has included the dubious pleasure of analyzing unknown samples in a laboratory class in qualitative organic analysis has probably synthesized a urethane. These are a group of commercially important materials with a functional group that results from the reaction of an isocyanate with an alcohol according to the reaction



Polyurethane elastomers are block copolymers built of relatively short urethane hard segments separating long, flexible, soft block segments. Polyurethanes normally possess microphase separation, with the soft blocks giving extensibility, while the hard blocks provide mechanical reinforcement. Polyurethanes can be compounded to give mechanical properties that are superior to those of conventional vulcanizates. The four main types of polyurethanes are casting resins, millable rubbers, semi-cured thermosetting resins, and thermoplastic materials. Many of the commercially available materials, as well as those studied in research laboratories, that have applications in underwater acoustics are casting resins and will be the subject of discussion here. Refs. 346 through 348 contain further information on the other types of materials.

A vast body of literature has been published dealing with the chemistry and synthesis of polyurethanes. Representative examples can be found in Refs. 215, 346 through 356. These include effects of molecular weight and structure of the soft-block polyol, structure and type of isocyanate, dimerization or trimerization of the isocyanate, and type of chain extender and crosslinker used. Here, we shall merely sketch the salient points of the formation of a polyurethane.

Polyurethane elastomers are normally formed from a bifunctional, medium-to-high molecular weight polyol, a bifunctional isocyanate, and a polyfunctional alcohol and/or amine. Many urethane syntheses involve the formation of a prepolymer, as shown in Fig. 11.1. The prepolymer is normally a polyol in the 1000- to 3000-molecular weight range that has been treated with an amount of isocyanate such that the polyol is terminated with NCO groups. The prepolymer is then treated with an alcohol or amine that acts as a crosslinking agent and also serves to extend the urethane chain linkage by coupling isocyanate-terminated units in the prepolymer to build up a polymer of high molecular weight. The mixing of the prepolymer and chain extender normally occurs at a sufficiently elevated temperature to provide low viscosity for mixing and under vacuum to remove dissolved and evolved gases. The mixture is then placed in a mold at a suitable temperature and cured for the necessary length of time. Post-cures may be necessary in some cases.

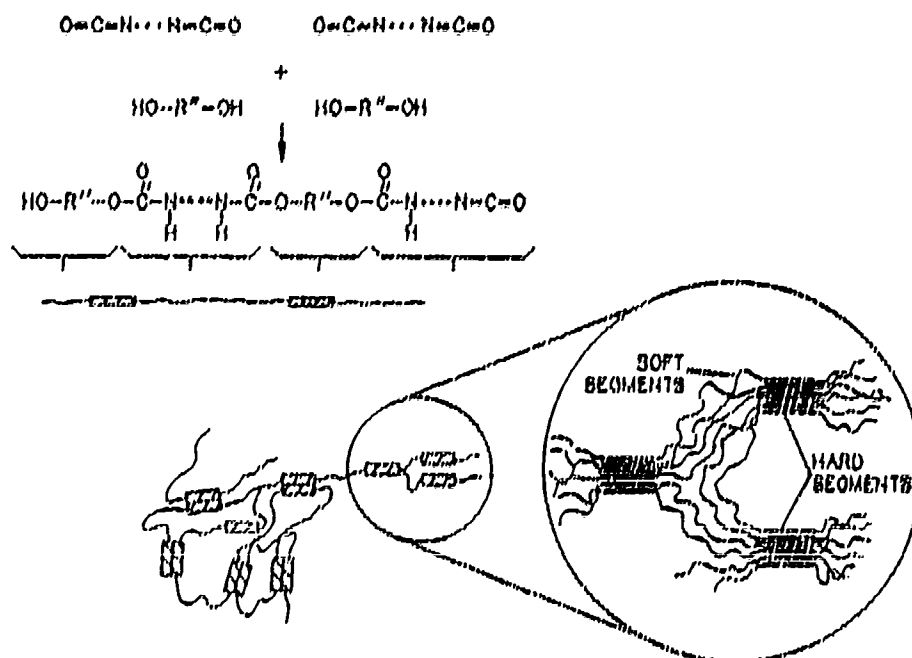


Fig. 11.1 - Schematic of formation of polyurethane.

A related procedure is the one-shot synthesis, in which polyol, diisocyanate, and curing agent are mixed and cast without using the prepolymer route. These polymers normally involve the use of all hydroxyl systems, or the use of suitable catalysts such as stannous octoate or dibutyl tin dilaurate to accelerate the hydroxyl-isocyanate reaction in preference to the amine-isocyanate reaction³⁴⁸.

The NCO group of the isocyanate moiety is highly reactive and capable of undergoing reactions with a variety of functional groups. The primary areas include: reaction with an alcohol to form a urethane, reaction with an amine to form a urea, reaction with water to form a urea, and reaction with an organic acid to form an amide. Excess isocyanate may undergo secondary reactions. These include reaction with a urethane to form an allophanate ester, reaction with a urea to form a biuret linkage, and reaction with an amide to form acylurea. These secondary reactions are responsible for the formation of chemical crosslinks in polyurethanes.

In addition to the reactions that may occur due to isocyanate groups, other polymerizable groups such as sites of unsaturation may be incorporated into one of the reacting segments. This increases the variety of structures, handling characteristics, and range of physical properties and applications of polyurethanes. Polyurethanes as a group normally have good electrical properties. They also have good tensile strength and shear resistance, as well as good abrasion resistance. Many urethanes have high damping and poor heat build-up characteristics, although this can be minimized through proper selection of reagents. Generalizations about solvent resistance are more difficult to make than for other types of elastomers, due to the wide variety of materials from which polyurethanes can be formed. Many polyurethanes do not survive well in direct sunlight or in contact with organic solvents.

Lequin and Weller^{357,358} have evaluated the long-term aging characteristics of a number of commercially available castable polyurethanes. Some of these same materials have been evaluated in this laboratory³⁵⁹ for compatibility with organic liquids that are sometimes used as acoustic coupling fluids in underwater acoustical systems. The

development of a castor oil-resistant polyurethane specifically designed for use as a sonar encapsulant has been described by Thompson and Maurice³⁶⁰.

11.2 COMMERCIALLY AVAILABLE MATERIALS

A number of commercially available liquid casting polyurethanes designed for use as electrical molding and potting compounds have been used for underwater acoustic applications. The majority of these materials are considered to be proprietary compounds, so that their exact compositions are unknown. In this section, we have tabulated available manufacturers' physical properties data and viscoelastic properties data (Figs. 11.2 through 11.20) for a number of these materials^{106,361}. The PR series is manufactured by Products Research and Chemicals, while the Conathane EN series is manufactured by Conap, Inc.

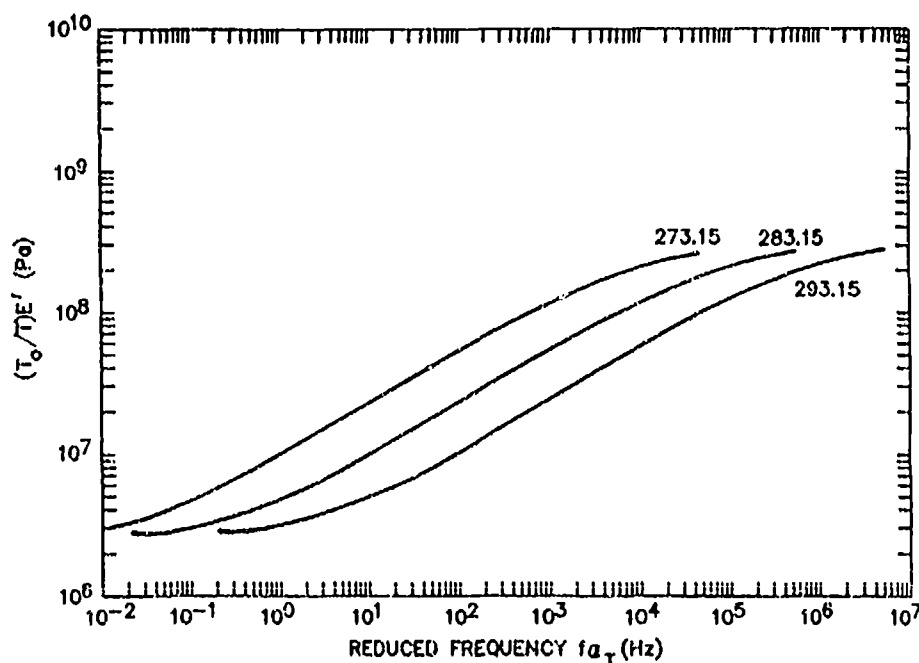


Fig. 11.2 -- Plot of storage Young's modulus vs reduced frequency at three different reference temperatures for PR 1526

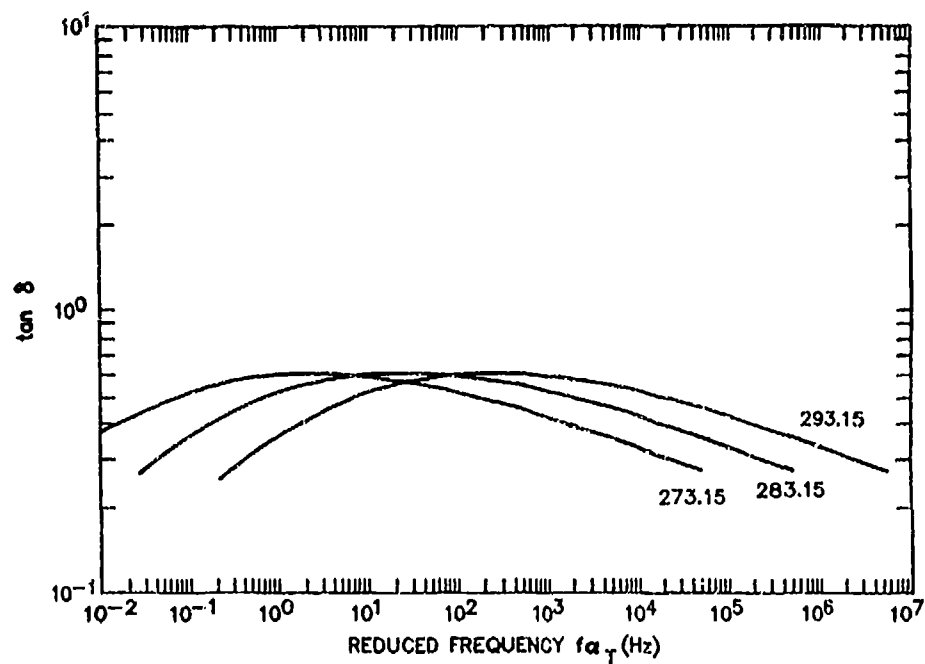


Fig. 11.3 - Plot of loss tangent vs reduced frequency at three different reference temperatures for PR 1520

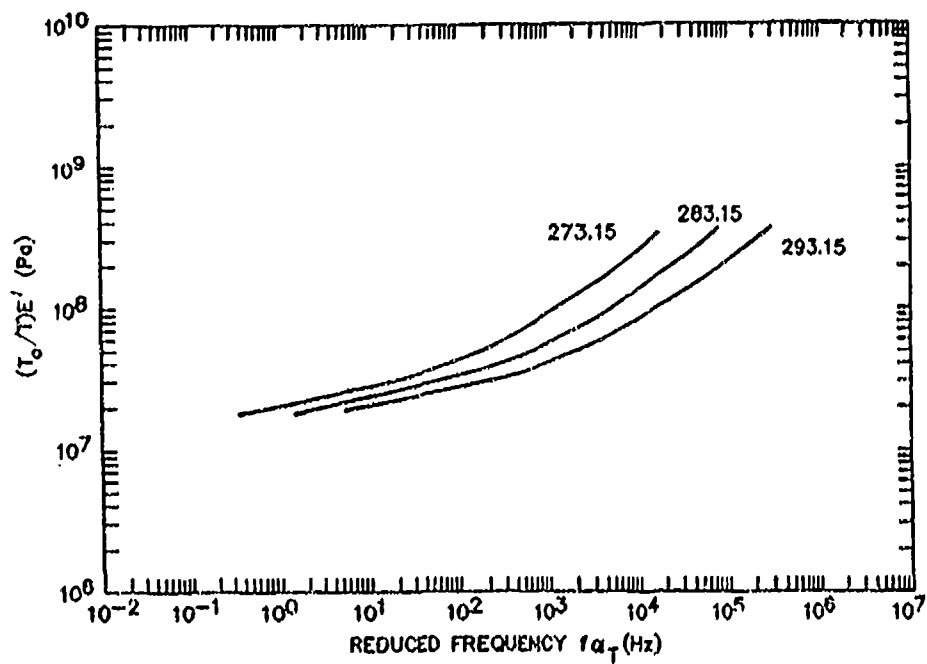


Fig. 11.4 - Plot of storage Young's modulus vs reduced frequency at three different reference temperatures for PR 1520

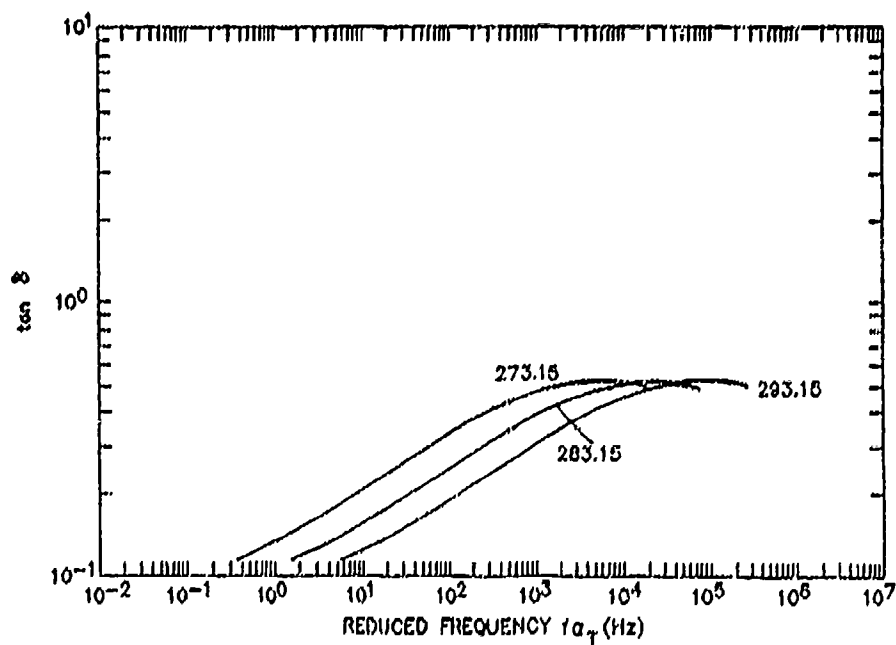


Fig. 11.5 - Plot of loss tangent vs reduced frequency at three different reference temperatures for PR 1528

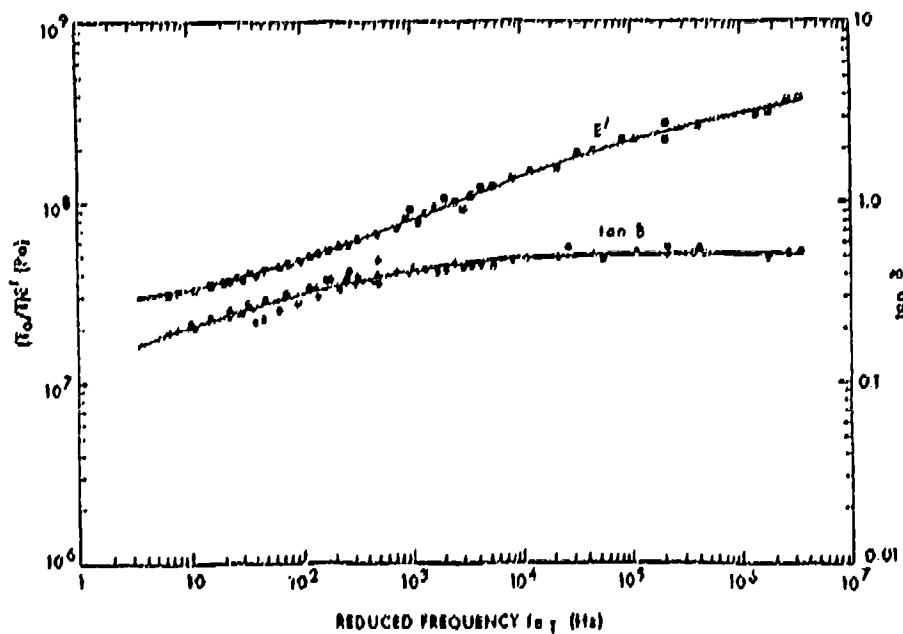


Fig. 11.6 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 293.15K for PR 1528

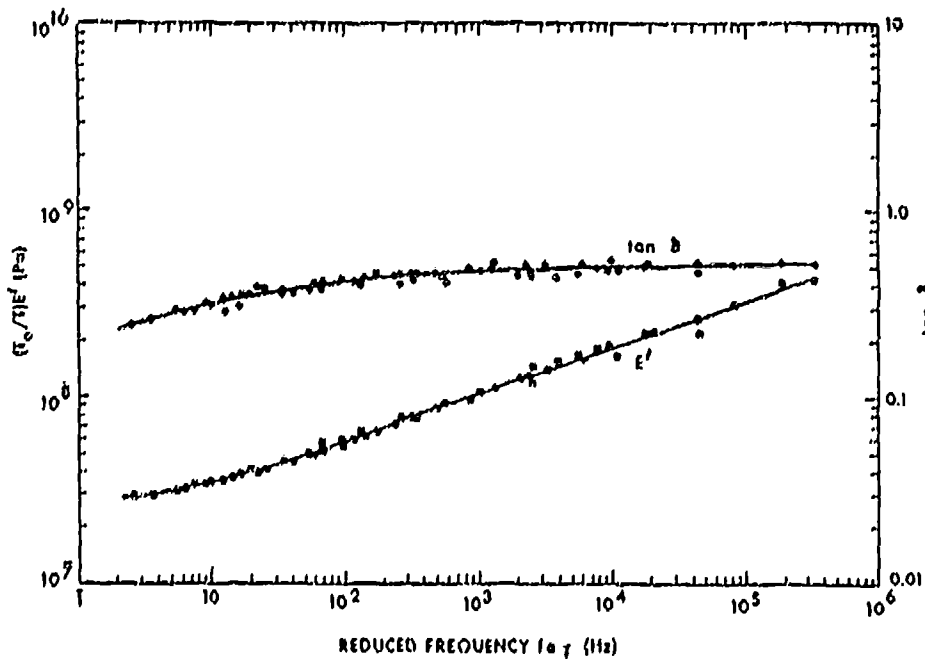


Fig. 11.7 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 288.15K for PR 1547

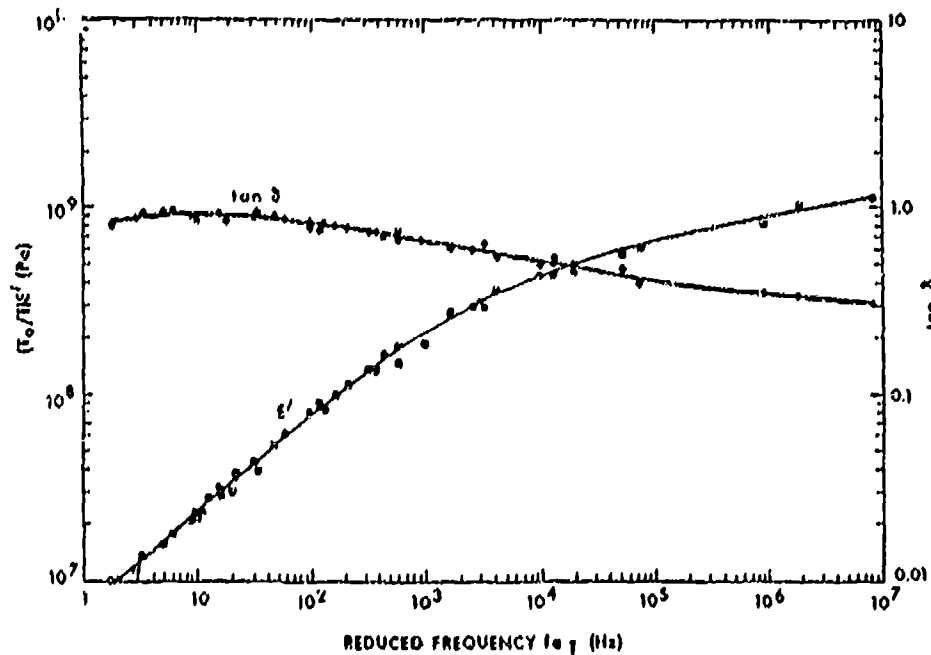


Fig. 11.8 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 288.15K for PR 1504

Elastomeric Materials for Acoustical Applications

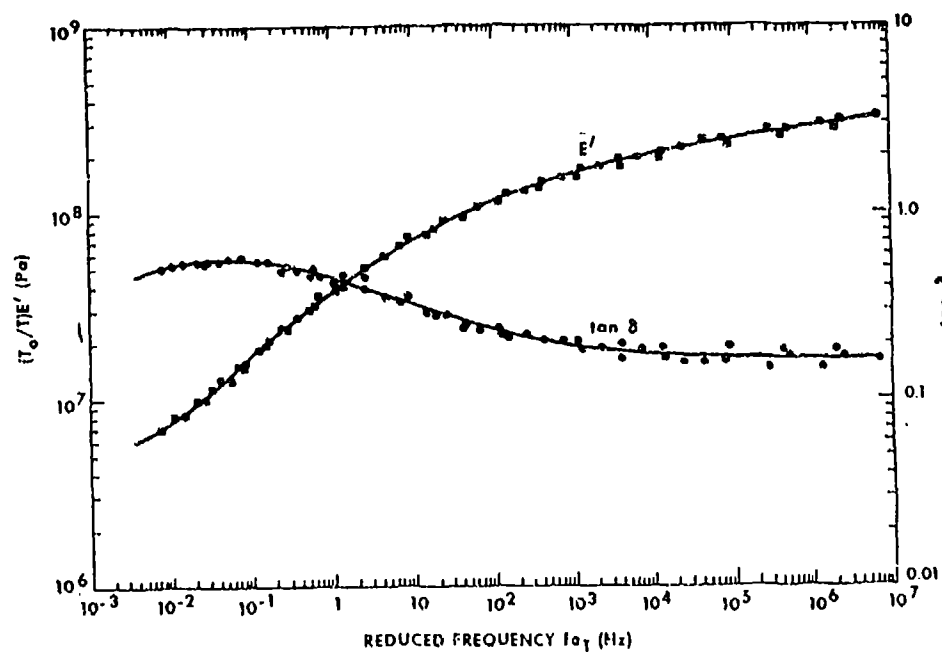


Fig. 11.9 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1576

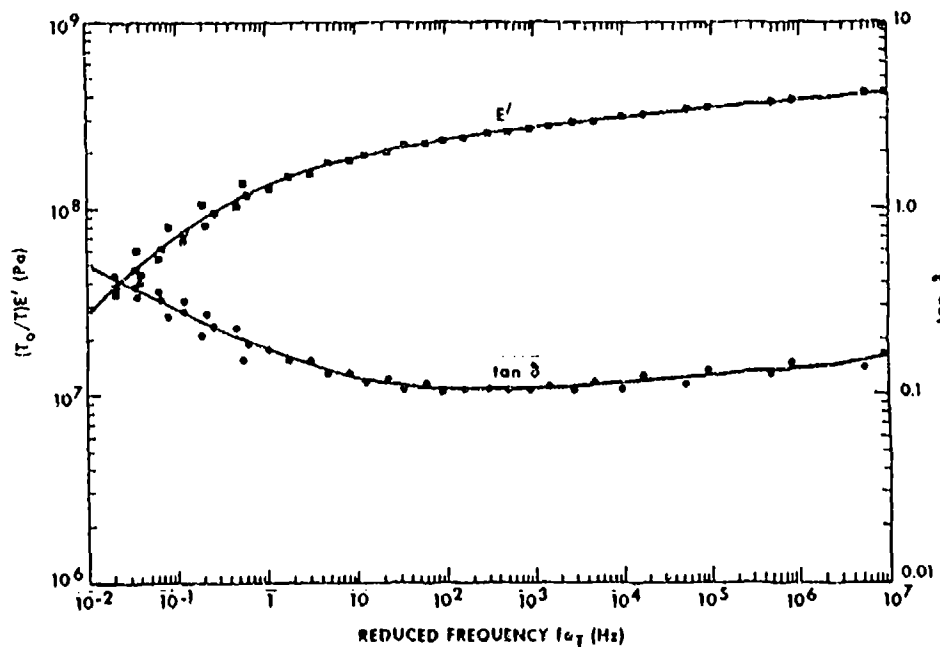


Fig. 11.10 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1574

11.2 Commercially Available Materials

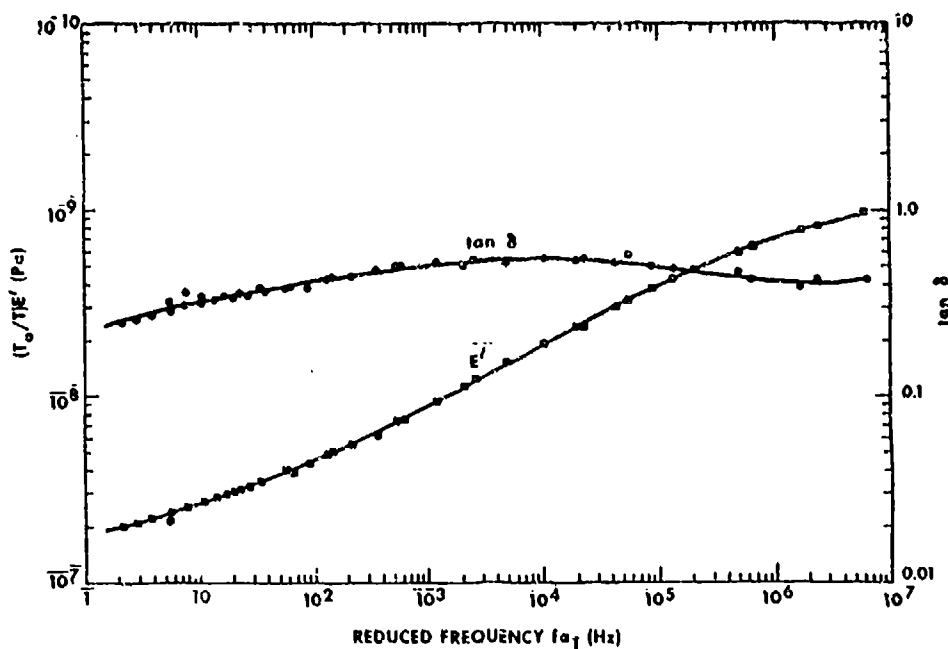


Fig. 11.11 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1598

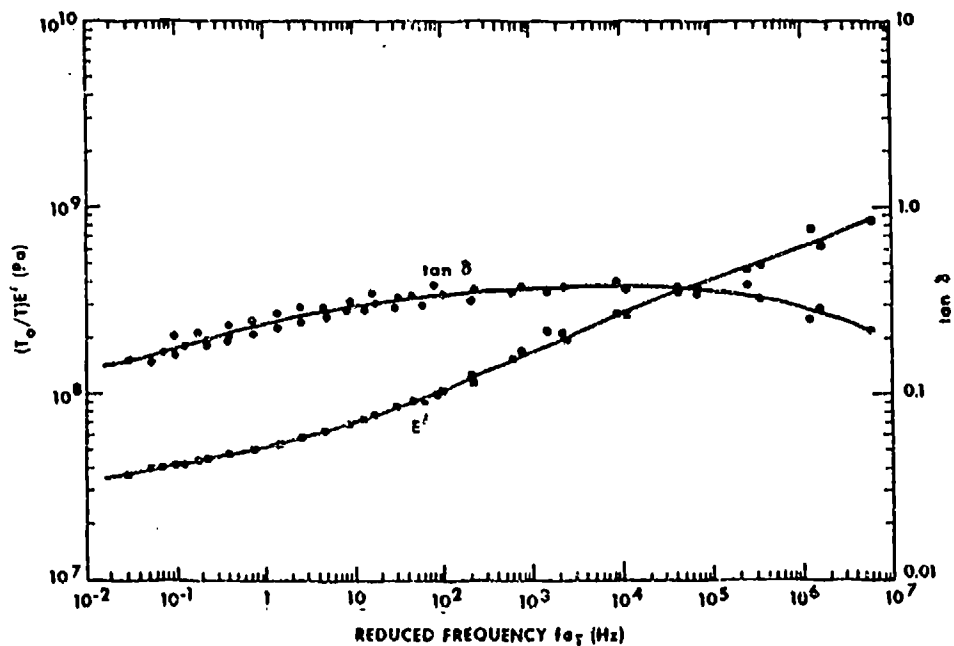


Fig. 11.12 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1592

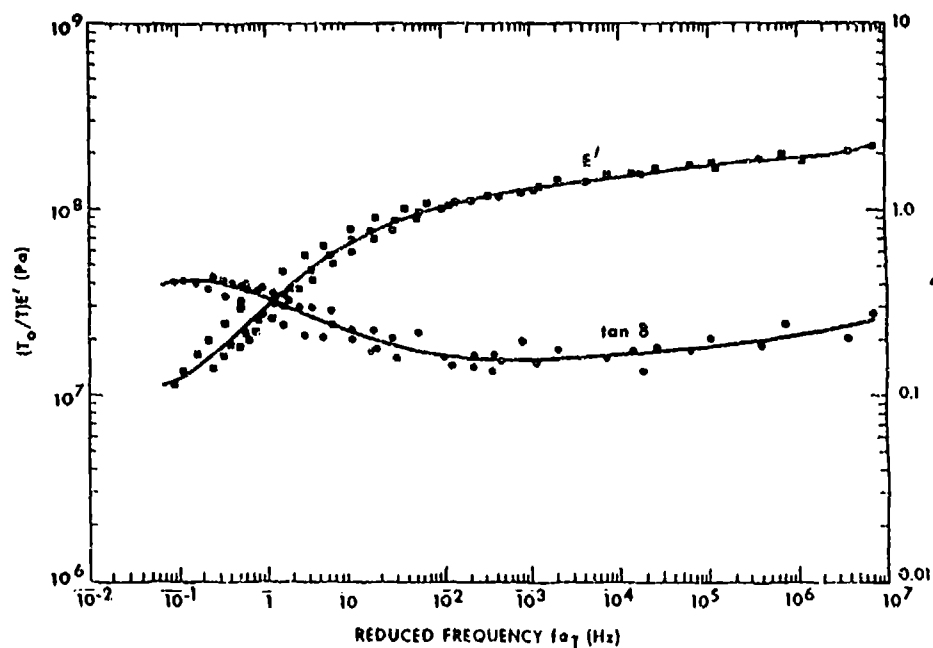


Fig. 11.13 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for EN 5

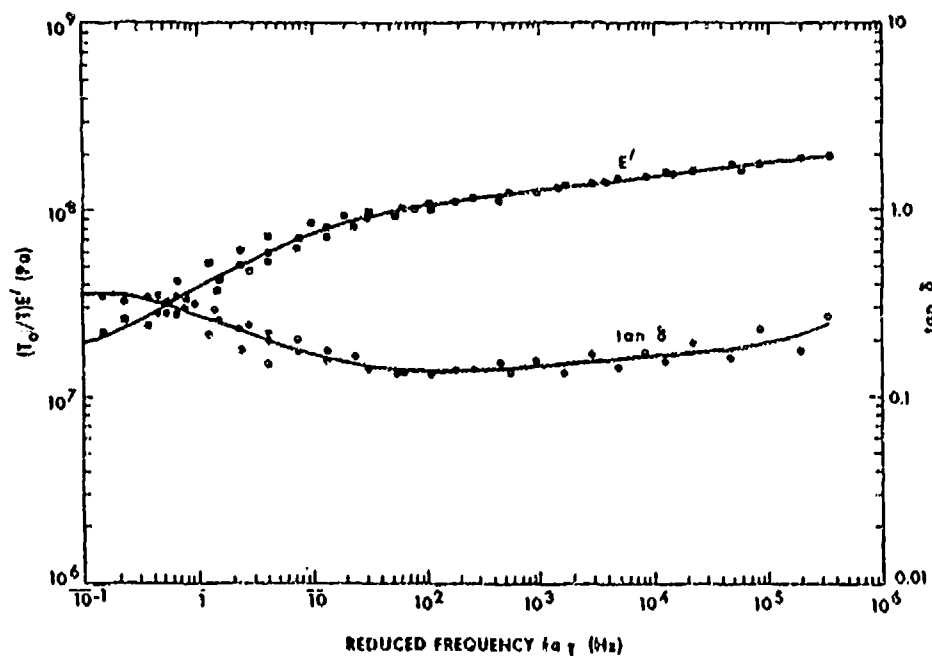


Fig. 11.14 - Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for EN 9

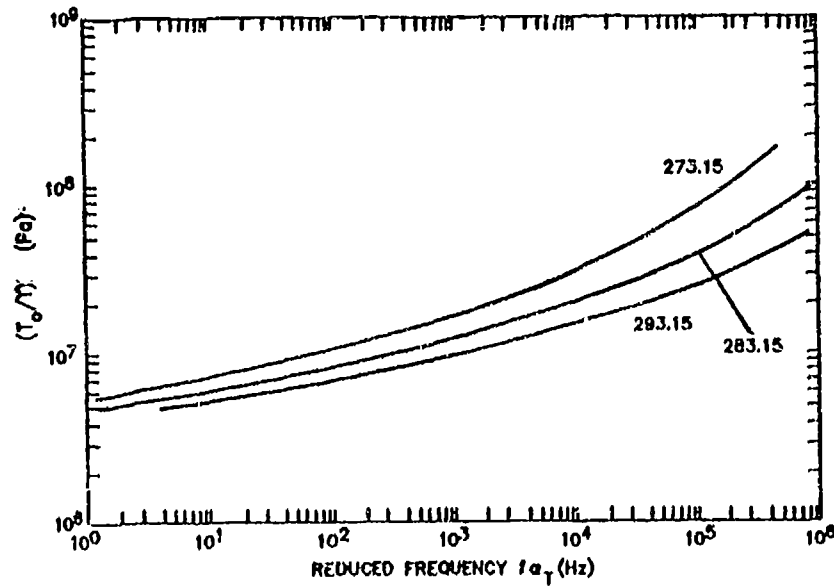


Fig. 11.15 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Uralite 8140

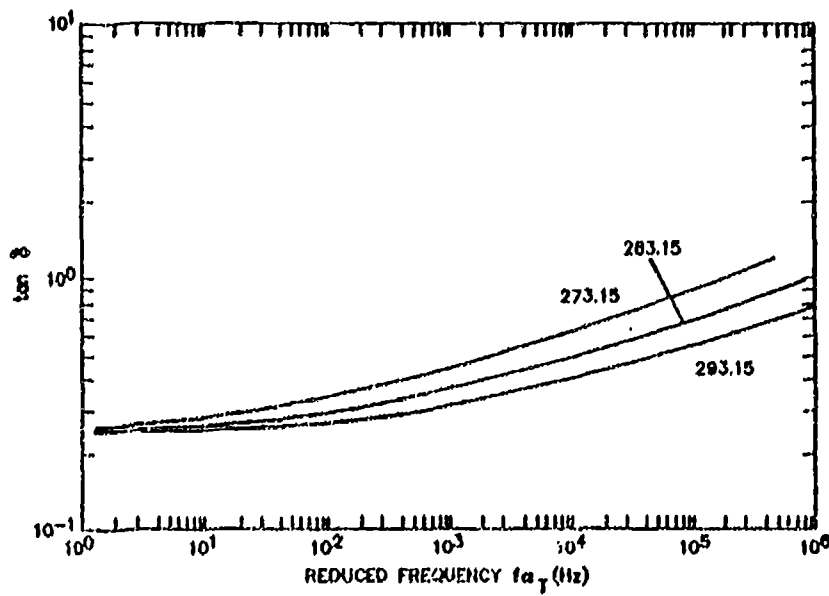


Fig. 11.16 - Plot of loss tangent vs reduced frequency at three temperatures for Uralite 8140

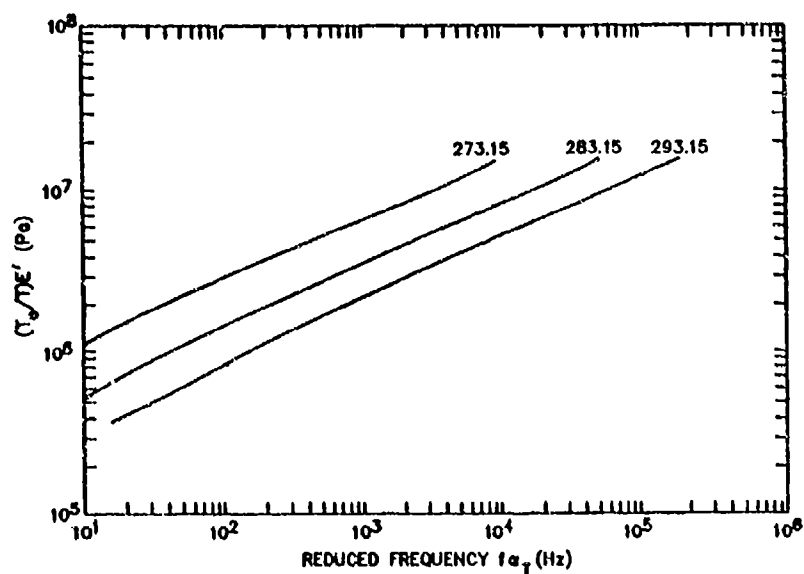


Fig. 11.17 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Sorbothane (55 Shore 00 durometer)

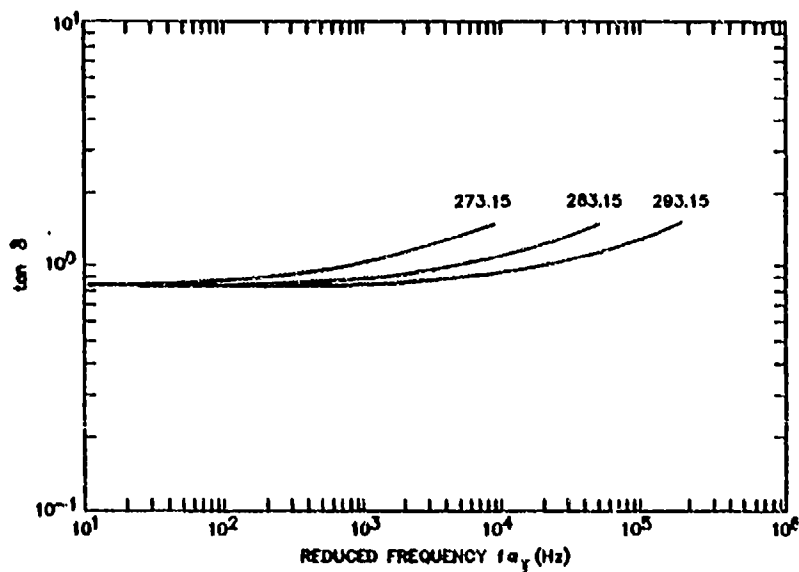


Fig. 11.18 - Plot of loss tangent vs reduced frequency at three temperatures for Sorbothane (55 Shore 00 durometer)

11.2 Commercially Available Materials

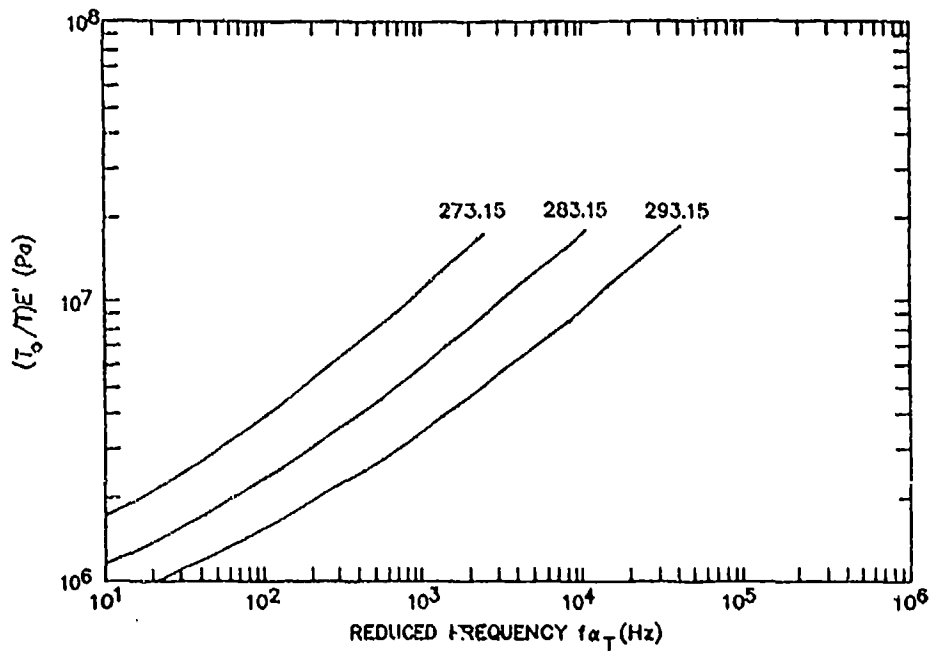


Fig. 11.19 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Sorbothane (70 shore 00 durometer)

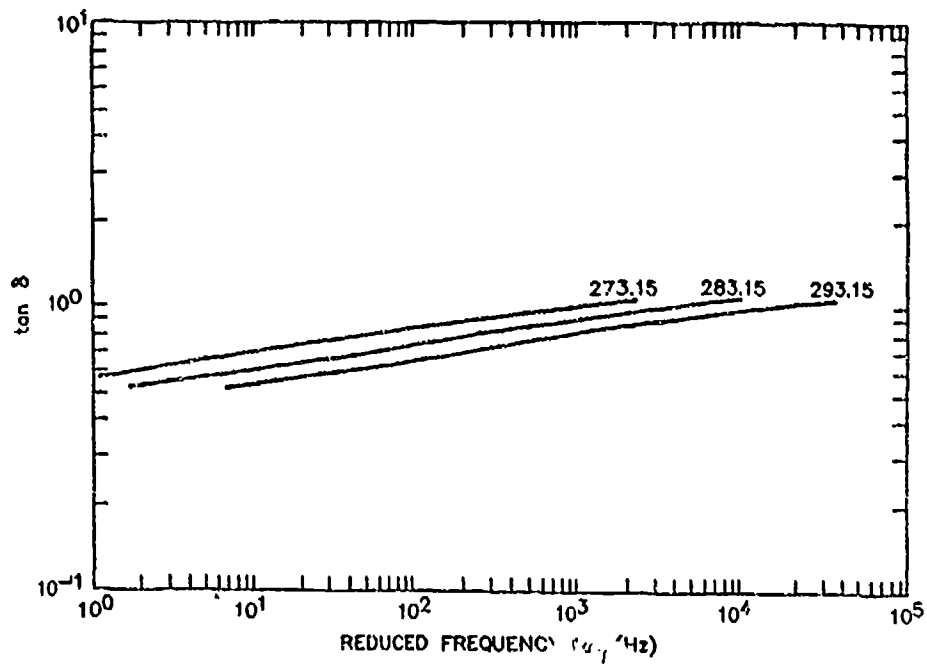


Fig. 11.20 - Plot of loss tangent vs reduced frequency at three temperatures for Sorbothane (70 shore 00 durometer)

Polyurethane PR 1526

GENERAL INFORMATION:

PR-1526 is a liquid, two-part, low-viscosity, medium-hardness polyurethane especially formulated for use as a molding compound in electrical applications that require outstanding retention of electrical properties under extremes of high humidity or total water immersion. It requires an elevated curing temperature for optimum performance properties. It contains no MOCA or TDI.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	60	
Tensile Strength	4.14	MPa
Ultimate Elongation	350	%
Tear Strength (Die C)	17.51	kN/m
Density	1000	kg/m ³
Dielectric Constant at 24°C		
1 kHz	3.7	
1 MHz	2.9	
Dielectric Strength		
(re 150 mils thickness)	350	V/mil
Volume resistivity at 24°C	7.1×10^{14}	ohm·cm

SHIFT PARAMETERS: $\log a_T = 8244 (1/T - 1/T_0)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	6.67817	-0.28975
a_1	0.25919	0.10244
a_2	0.054916	-0.041264
a_3	-0.0087682	0.0026472
a_4	1.0652×10^{-4}	0

*Polyurethane PR 1528***GENERAL INFORMATION:**

PR-1528 is a liquid, two-part, medium-hardness, low-viscosity polyurethane especially formulated to yield a tough, flexible elastomer with excellent resistance to weathering, cold flow, and moisture. It contains no MOCA.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	67	
Tensile Strength	17.2	MPa
Ultimate Elongation	615	%
Tear Strength (Die C)	12.4	kN/m
Density	1050	kg/m ³
Compression Set (ASTM D395, Method B)	39 at 24°C	%
Dielectric Constant at 24°C		
1 kHz	7.2	
1 MHz	4.6	
Dielectric Strength (re 125 mils thickness)	285	V/mil
Volume resistivity at 24°C	1.5×10^{12}	ohm·cm

SHIFT PARAMETERS: $\log a_T = 4827 (1/T - 1/T_0)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.24817	-0.98045
a_1	0.17050	0.10854
a_2	-0.059443	0.054603
a_3	0.026226	-0.010140
a_4	-0.0020499	0

Polyurethane PR 1538

GENERAL INFORMATION:

PR-1538 is a liquid, two-part polyurethane formulated for use as a low-viscosity potting compound for electrical connectors, a molding compound for electrical cables and mechanical parts, a circuit-board coating, and an electrical imbedding compound. It is a MOCA-cured system.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	80	
Tensile Strength	20.9	MPa
Ultimate Elongation	600	%
Tear Strength (Die C)	35.01	kN/m
Density	1120	kg/m ³
Compression Set (ASTM D295, Method B)	10 at 24°C	%
Dielectric Constant at 24°C		
1 kHz	6.8	
10 kHz	6.2	
1 MHz	4.4	
Water Permeability	4220	10 ⁻¹⁰ g H ₂ O -cm/cm ² /hr/torr
Dielectric Strength (re 125 mils thickness)	278	V/mil
Coefficient of Thermal Expansion	4.50x10 ⁻⁴	cm/cm/°C
Useful Temperature Range	-57 to 140°C	

SHIFT PARAMETERS: $\log a_T = -4.50(T - 283.15) / (42.5 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.47787	-0.95501
a_1	-0.083002	0.20545
a_2	0.12708	-0.040808
a_3	-0.020829	0.0017057
a_4	0.0010590	0

*Polyurethane PR 1547***GENERAL INFORMATION:**

PR-1547 is a liquid, two-part polyurethane formulated for use as a molding compound for electrical cables and/or a potting compound for electrical connectors where resistance to cold flow, flexibility, high tensile strength, and exposure from -57 to 149°C are required. It is a MOCA-cured system.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	80	
Tensile Strength	20.7	MPa
Ultimate Elongation	600	%
Tear Strength (Die C)	43.76	kN/m
Density	1050	kg/m ³
Compression Set (ASTM D395, Method B)	54 at 24°C	%
Dielectric Constant at 24°C:		
1 kHz	5.8	
1 MHz	4.7	
Dielectric Strength (re 125 mils thickness)	300	V/mil

SHIFT PARAMETERS: $\text{Log } a_T = -6.34(T - 283.15) / (48.6 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.4586	-0.70840
a_1	-0.040755	0.26203
a_2	0.15001	-0.058489
a_3	-0.032003	0.0045039
a_4	0.0023867	0

*Polyurethane PR 1564***GENERAL INFORMATION:**

PR-1564 is a liquid, two-part polyurethane formulated for use as a low-viscosity potting compound for electrical connectors or a molding compound for electrical cables in cases where moderate Shore A hardness, resistance to cold flow, extra flexibility, and exposure from -62 to +135 °C are required. PR-1564 contains no MOCA.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C).

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	65	
Tensile Strength	6.90	MPa
Ultimate Elongation	300	%
Tear Strength (Die C)	14.1	kN/m
Density	1060	kg/m ³
Dielectric Constant at 24°C:		
1 kHz	7.0	
1 MHz	4.3	
Dielectric Strength (re 125 mils thickness)	335	V/mil
Volume Resistivity	1.0x10 ¹²	ohm·cm

SHIFT PARAMETERS: $\log a_T = -6.77(T - 283.15) / (45.1 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	6.8670	-0.075553
a_1	0.44638	0.076665
a_2	0.082181	-0.0049657
a_3	-0.029611	0.0042828
a_4	0.0021756	0

*Polyurethane PR 1570***GENERAL INFORMATION:**

PR-1570 is liquid, two-part polyurethane formulated for use as a medium hardness potting compound for use in cases where outstanding retention of electrical properties is desired under conditions of high humidity and temperature. It is a non-MOCA cured system.

TYPICAL PHYSICAL PROPERTIES (Cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	75	
Tensile Strength	6.90	MPa
Ultimate Elongation	350	%
Tear Strength (Die C)	17.5	kN/m
Density	980	kg/m ³
Compression Set (ASTM D395, Method B)	28 at 24°C	%
Dielectric Constant at 24°C:		
1 kHz	3.2	
1 MHz	2.7	
Dielectric Strength (re 125 mils thickness)	335	V/mil
Water Permeability (10 ⁻¹⁰ g H ₂ O cm/cm ² -hr-torr)	900	
Sound Speed (seawater, 20°C, 200 kHz)	1581	m/sec

SHIFT PARAMETERS: $\text{Log } \alpha_T = -14.7(T - 283.15) / (93.8 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus</u>	<u>Tan δ</u>
a_0	7.5643	-0.34906
a_1	0.30828	-0.12828
a_2	-0.025078	-0.021014
a_3	-0.0032733	0.01070
a_4	0.00049629	-0.0010998
a_5	0	2.5259×10^{-6}

Polyurethane PR 1574

GENERAL INFORMATION:

PR-1574 is liquid, two-part polyurethane formulated for use as a low-viscosity, high-hardness potting or molding compound for use in cases where outstanding retention of electrical properties is desired under conditions of high humidity and temperatures. It does not contain MOCA.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	90	
Tensile Strength	17.2	MPa
Ultimate Elongation	425	%
Tear Strength	52.50	kN/m
Density	1000	kg/m ³
Dielectric Constant at 24°C		
1 kHz	2.8	
1 MHz	2.8	
Dielectric Strength		
(re 125 mils thickness)	330	V/mil
Volume Resistivity	1.0×10^{16}	ohm·cm
Water Permeability		
(10^{-10} g H ₂ O cm/cm ² -cm-torr)	900	

SHIFT PARAMETERS: $\log a_T = -13.4(T - 283.15) / (90.2 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus</u>	<u>Tan δ</u>
a_0	8.1188	-0.75423
a_1	0.20413	-0.16961
a_2	-0.054095	0.039363
a_3	0.0086145	-0.0022824
a_4	-5.1135×10^{-4}	0

*Polyurethane PR 1590***GENERAL INFORMATION:**

PR-1590 is liquid, two-part polyurethane formulated for use as a low-viscosity potting compound for electrical connectors and as a molding compound for electrical cables where the following are required: a medium-hardness, resistance to cold flow, and prolonged exposure to extreme temperature. PR-1590 is a MOCA-free compound.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	75	
Tensile Strength	15.2	MPa
Ultimate Elongation	500	%
Tear Strength	30.63	kN/m
Density	1100	kg/m ³
Volume Resistivity	1.0x10 ¹²	ohm·cm
Dielectric Constant at 24°C		
1 kHz	7.4	
1 MHz	4.8	
Dielectric Strength (re 125 mils thickness)	300	V/mil

SHIFT PARAMETERS: $\text{Log } a_T = -8.53(T - 283.15) / (95.5 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus</u>	<u>Tan δ</u>
a_0	7.2656	-0.65962
a_1	0.11062	0.19348
a_2	0.046066	-0.025368
a_3	-0.0012692	3.2300x10 ⁻⁴
a_4	-0.00035692	0

*Polyurethane PR 1592***GENERAL INFORMATION:**

PR-1592 is a liquid, two-part polyurethane that is especially formulated for use as a high-hardness potting compound for electrical connectors and as a molding compound for electrical cables where high tensile strength, resistance to cold flow, and prolonged exposure to extreme temperature are required. PR-1592 is a KOCA-free compound.

TYPICAL PHYSICAL PROPERTIES (cured 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	85	
Tensile Strength	41.4	MPa
Ultimate Elongation	425	%
100% Modulus	4.14	MPa
Tear Strength	55.43	kN/m
Density	1100	kg/m ³
Volume Resistivity	1.0×10^{12}	ohm·cm
Dielectric Constant at 24°C		
1 kHz	6.5	
1 MHz	4.6	
Dielectric Strength (re 125 mils thickness)	300 V/mil	

SHIFT PARAMETERS: $\log a_T = -12.9(T-283.15) / (107 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.71248	-0.62953
a_1	0.12531	0.10910
a_2	0.021141	-0.011586
a_3	-0.0018216	-6.8577×10^{-4}
a_4	-2.1893×10^{-5}	0

*Polyurethane EN 5 (Conathane)***GENERAL INFORMATION:**

EN-5 is a two-component, liquid, polyurethane potting, casting, and molding system. The cured elastomer exhibits outstanding hydrolytic stability, stable electrical properties, thermal shock properties, and good handling properties. It is a MOCA-free system.

TYPICAL PHYSICAL PROPERTIES (cured 7 days at 25°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	85	
Tensile Strength	13.4	MPa
Ultimate Elongation	520	%
100% Modulus (97°C at 95% RH)	5.52	MPa
300% Modulus (97°C at 95% RH)	8.96	MPa
Density	1000	kg/m ³
Volume Resistivity	2.1×10 ⁵	ohm·cm

SHIFT PARAMETERS: $\text{Log } a_T = -7.52(T - 283.15) / (57.5 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.4813	-0.48036
a_1	0.37315	-0.17770
a_2	-0.050068	-0.037845
a_3	-0.0018623	0.038614
a_4	5.8219×10 ⁻⁴	-0.0074981
a_5	0	4.6309×10 ⁻⁴

*Polyurethane EN 9 (Conathane)***GENERAL INFORMATION:**

EN-9 is a two-component, liquid, polyurethane potting, casting, and molding system. The cured elastomer exhibits outstanding hydrolytic stability, stable electrical properties, thermal shock properties, and good handling properties. It is a MOCA-free system.

TYPICAL PHYSICAL PROPERTIES (cured for 16 hrs at 82°C):

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	85	
Tensile Strength	17.2	MPa
Ultimate Elongation	400-500	%
100% Modulus	3.45-6.21	MPa
300% Modulus	8.28-12.8	MPa
Density	1010	kg/m ³
Volume Resistivity	3.42×10^{15}	ohm·cm

SHIFT PARAMETERS: $\log a_T = -10.3(T - 283.15) / (95.6 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	7.6025	-0.56005
a_1	0.29905	-0.22409
a_2	-0.042988	-0.044149
a_3	-0.0020213	0.068664
a_4	7.5343×10^{-4}	-0.017250
a_5	0	0.0013640

*Polyurethane Hexcel Uralite 3140***GENERAL INFORMATION:**

Uralite 3140 is a two-component, liquid, polyurethane casting system. The cured elastomer exhibits outstanding hydrolytic stability, stable electrical properties, and good handling properties. It is a MOCA-free system.

TYPICAL PHYSICAL PROPERTIES (cured 4 hrs at 25°C, 4-hr post cure at 82°C)

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	60	
Tensile Strength	7.07	MPa
Ultimate Elongation	700	%
Tear Strength	45.5	kN/m
Density	1073	kg/m ³

SHIFT PARAMETERS: $\text{Log } a_T = 4673 (1/T - 1/T_0)$

<u>Coefficient</u>	<u>Modulus (283.15)</u>	<u>Tan δ (283.15K)</u>
a_0	6.6659	-0.62058
a_1	0.092864	-0.0034600
a_2	0.023520	0.022952
a_3	-0.0048540	-0.00087312
a_4	0.00076043	0

*Polyurethane Sorbothane (Shore 00, 50, and 70 Durometer)***GENERAL INFORMATION:**

Sorbothane is a unique type of polyurethane that is based upon propylene oxide evolving chains of very low and very high molecular weight³⁵⁹. It is a solid material, yet possesses easy distortion, a memory of shape, delayed recovery, and the ability to cope with torsional loading. These properties are typically associated with a viscous liquid, yet Sorbothane has the dimensional stability of a solid. It has a very large capability to dissipate energy and has found applications in acoustical damping, vibration isolation, and shock absorption. It retains its damping capability over very wide temperature and frequency ranges. However, Sorbothane possesses a very low resistance to tear, with the resistance increasing as hardness increases. It has fair abrasion resistance in the upper hardness ranges. Sorbothane has good resistance to ultraviolet light, diesel oil, and kerosene. It is not inherently ozone resistant but can be compounded for this property. It has fair water-absorption characteristics. Sorbothane is safe for prolonged skin contact and can be provided in a variety of shapes and colors. It can be compounded to cover a range of Shore 00 values from 20 through 70. Sorbothane is marketed in the U. S. by Hamilton Kent, Kent, OH.

TYPICAL PHYSICAL PROPERTIES (Ref. 361):

<u>PARAMETERS</u>	<u>VALUE</u>		<u>UNITS</u>
Shore 00 Hardness	50	70	
Tensile Strength	0.83	1.24	MPa
Ultimate Elongation	560	300	%
Tear Strength	4.11	6.36	kN/m ³
Density	1073	1073	kg/m ³

SHIFT PARAMETERS: $\log a_T = -c_1 (T - 283.15) / (c_2 + T - 283.15)$

c_1	5.33	4.58
c_2	79.4	66.3
<u>Coefficient</u>	<u>Modulus (283.15K)</u>	
a_0	5.3326	5.7159
a_1	0.31920	0.16401
a_2	0.11249	0.16169
a_3	-0.038478	-0.050155
a_4	0.0038581	0.0053695
	<u>Tan δ (283.15K)</u>	
a_0	-0.077098	-0.36416
a_1	-0.0021978	0.17401
a_2	-0.010897	-0.034386
a_3	0.0048591	0.0037035

CHAPTER 12

OTHER CLASSES OF RUBBER

This section is intended to provide information on three other classes of elastomers for which there is either insufficient data available to justify a separate chapter or which do not find much application in underwater acoustics. However, these materials are of commercial importance. These are polybutadiene, Hypalon, and styrene-butadiene. In addition to the general discussion, specific formulations and viscoelastic property data given in Tables 12.1 through 12.3 and Figs. 12.1 through 12.6.

12.1 POLYBUTADIENE (BR)

Polybutadiene is a homopolymer of butadiene³⁶². It can be prepared in either a solution or an emulsion polymerization system. Polybutadienes in commercial production are 1,4 polymers produced through solution polymerization using Zeigler-type catalysts to give a high content of cis-structure. Polybutadienes with a high cis-structure are characterized by low hysteresis, excellent dynamic properties, and superior abrasion resistance^{362,363}. Those with a high trans-structure have high hardness, thermoplasticity, and poor hysteresis. Polybutadienes with an intermediate cis-structure (normally about 40 to 50%) are amorphous, possess intermediate properties, and have good low-temperature flexibility.

Polybutadiene can be vulcanized with common curing agents. Thiazoles and sulfenamides are commonly used. The rate of cure is similar to SBR, but slower than NR.

Polybutadiene (cis) is often mixed with other elastomers for commercial applications. It is commonly used commercially in tire tread, hose, tubing, soles, and equipment mounts, due to its abrasion resistance and high resilience. Polybutadiene is compatible in all proportions with NR, SBR, and neoprene. It does not blend as well with the more highly polar NBR elastomers and is normally restricted to 25 to 30% composition in these blends³⁶².

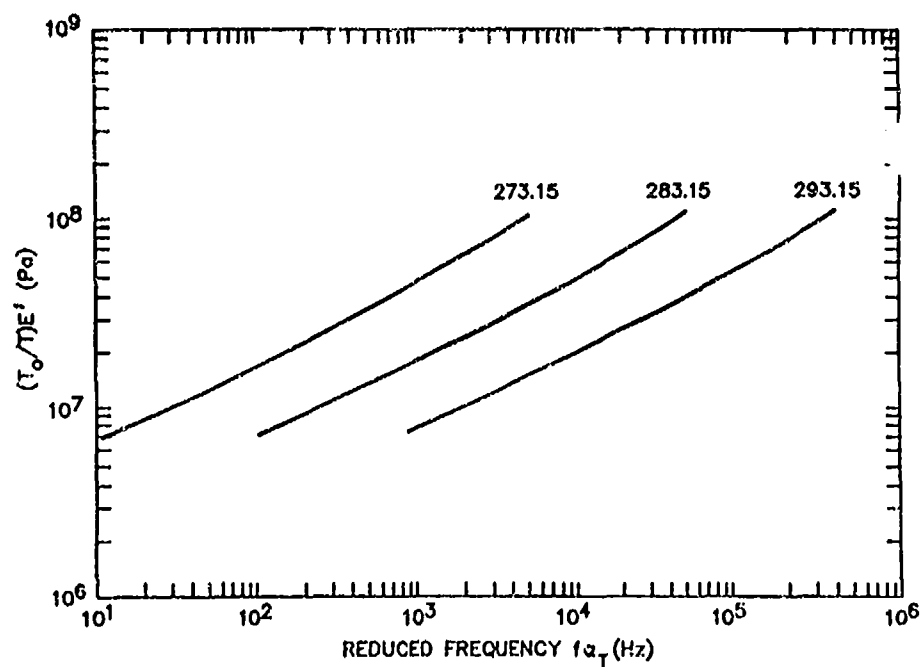


Fig. 12.1 - Plot of storage Young's modulus vs reduced frequency at three temperatures for polybutadiene

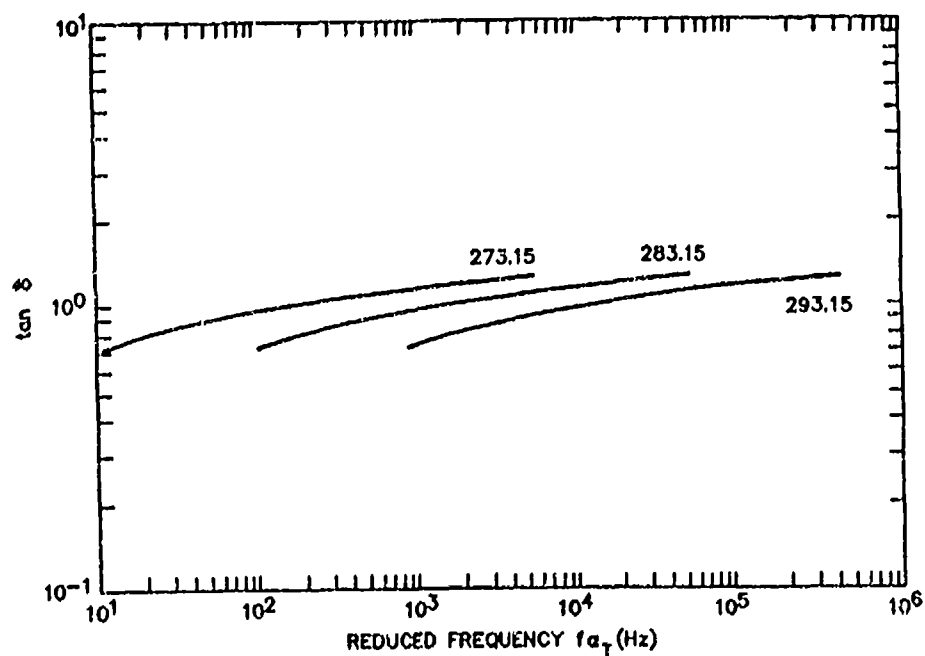


Fig. 12.2 - Plot of loss tangent vs reduced frequency at three temperatures for polybutadiene

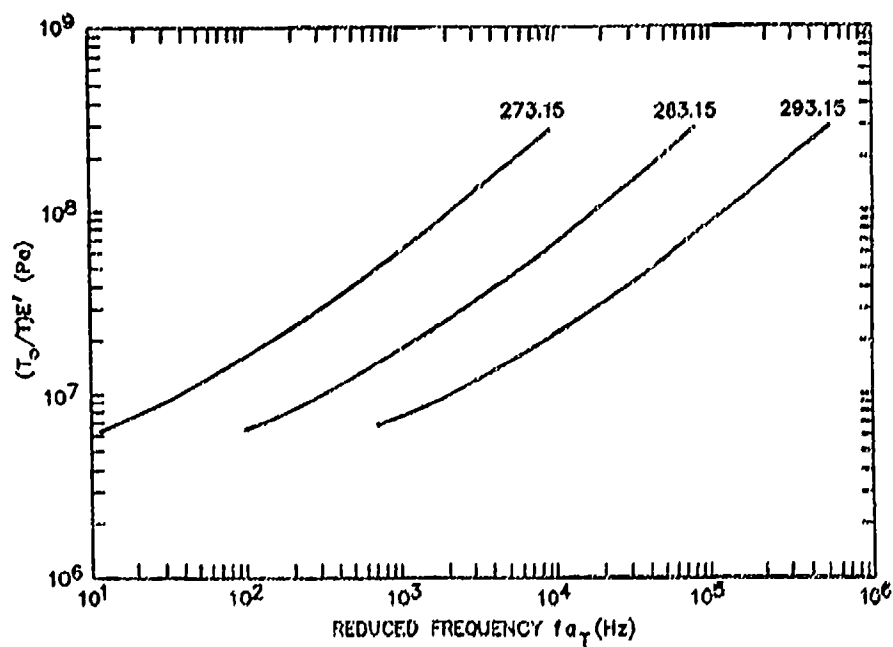


Fig. 12.3 - Plot of storage Young's modulus vs reduced frequency at three temperatures for Hypalon 48

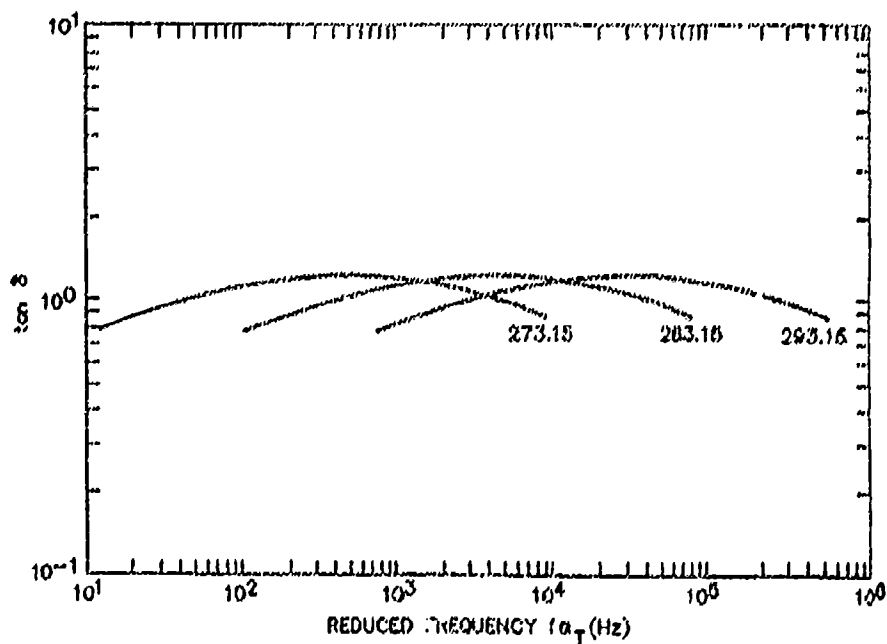


Fig. 12.4 - Plot of loss tangent vs reduced frequency at three temperatures for Hypalon 48

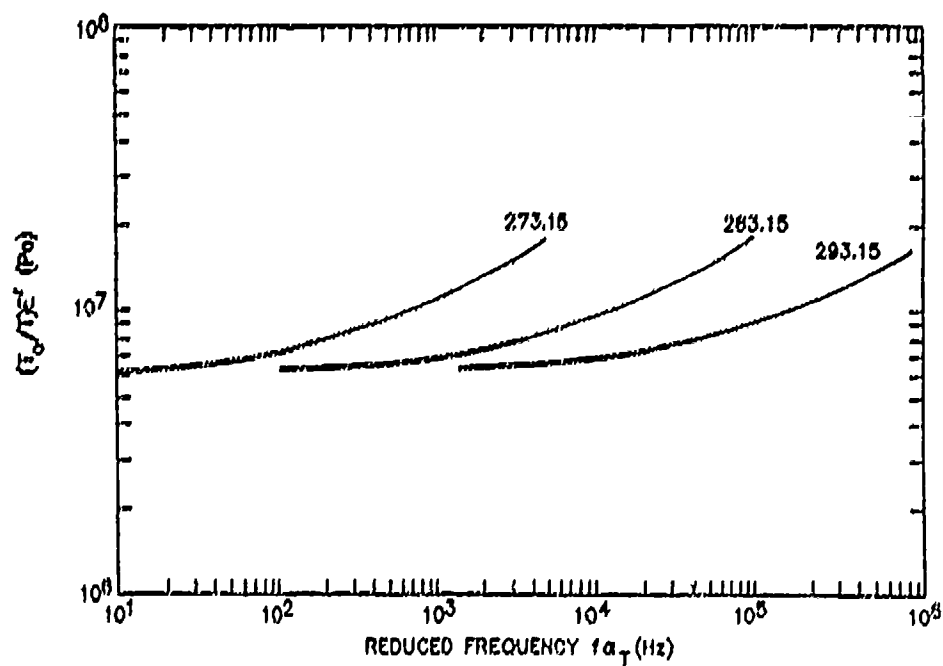


Fig. 12.5 - Plot of storage Young's modulus vs reduced frequency at three temperatures for styrene butadiene formulation AA 105-8

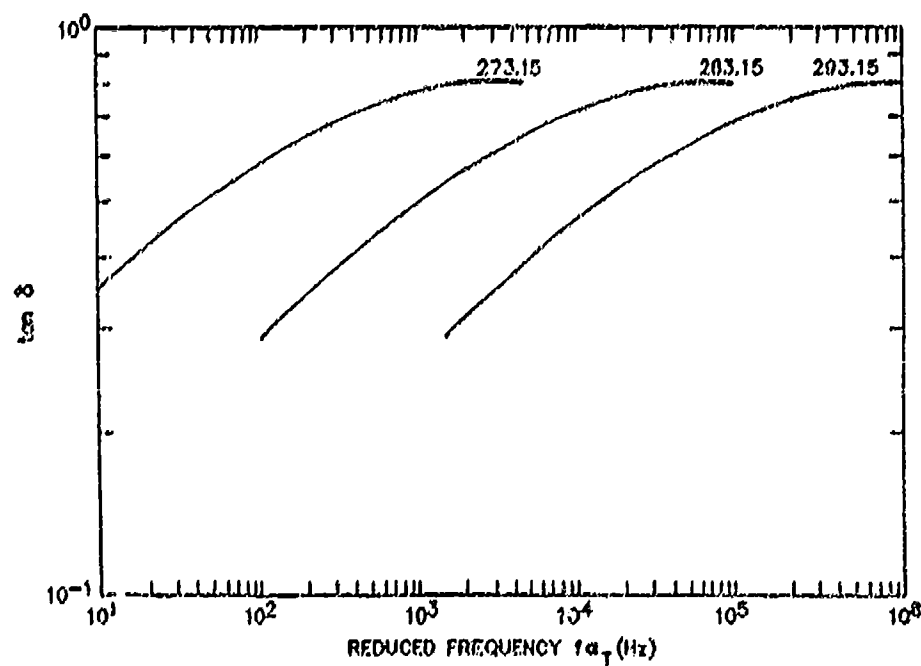


Fig. 12.6 - Plot of loss tangent vs reduced frequency at three temperatures for styrene butadiene formulation AA 105-8

TABLE 12.1 - POLYBUTADIENE FORMULATION³²⁵**FORMULATION:**

<u>COMPONENT</u>	<u>PHR</u>
Polybutadiene (62% Vinyl content)	100.0
FEF Carbon Black	55.0
Piccoumaron XX100	10.0
Aromatic Processing Oil (Dutrex 726)	5.0
Sulfur, rubber grade	5.0
Magnesium Oxide (Elastomag 100)	3.7
Calcium Oxide (Hydrated Lime 43)	1.7
Santocure NS	0.9
Methyl Tuads	0.2

Total parts by weight = 181.5

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Density	1127.0	kg/m ³
Cure Temperature	150	°C
90% Cure Time	25 - 30	min.

SHIFT PARAMETERS: $\text{Log } a_T = -37.5(T - 283.15) / (392 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	5.9199	-0.65629
a_1	0.56327	0.35721
a_2	-0.075804	-0.056763
a_3	0.013357	0.0032117
a_4	-4.8737×10^{-4}	0

TABLE 12.2 - HYPALON FORMULATION CB-165-3³³⁹

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
Hypalon 40	100.0
TE-28-G9	1.5
Sterling N774	20.0
Circosil 4240	10.0
Fyrol CEF	10.0
Califlux 510	15.0
DPFA 0053	3.0
Prespersion B1631	15.0
Sulfur	1.0
Unads	1.0

Total parts by weight = 176.5

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Shore A Hardness	48	
Tensile Strength	19.8	MPa
Ultimate Elongation	450	%
300% Modulus	7.38	MPa
Density	1290.0	kg/m ³
Cure Temperature	155	°C
Cure Time	20	min.

SHIFT PARAMETERS: $\text{Log } a_T = -17.67(T - 283.15) / (195.1 + T - 283.15)$

<u>Coefficient</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15)</u>
a_0	6.5945	-0.75722
a_1	-0.16382	0.37973
a_2	0.155730	-0.016701
a_3	-0.010178	-0.0064682
a_4	0.00025069	0

TABLE 12.3 - SBR FORMULATION²³⁹ AA-165-8

FORMULATION:

<u>COMPONENT</u>	<u>PHR</u>
Synpol 1500	100.0
Philblack N-550	30.0
Califlux 510	15.0
Protox 168	5.0
Stearic Acid	2.0
Sulfur	2.0
Methyl Tuads	0.5

Total parts by wt. = 154.4

STATIC PHYSICAL PROPERTIES:

<u>PARAMETERS</u>	<u>VALUE</u>	<u>UNITS</u>
Sho. A Hardness	51	
Tensile Strength	18.3	MPa
Ultimate Elongation	670	%
300% Modulus	5.86	MPa
Density	1095.0	kg/m ³
Cure Temperature	155	°C
90% Cure Time	15	min.

SHIFT PARAMETERS: $\log a_T = -16.97 (T - 283.15) / (136.3 + T - 283.15)$

<u>Coefficients</u>	<u>Modulus (283.15K)</u>	<u>Tan δ (283.15K)</u>
a_0	6.5912	-1.1234
a_1	0.26471	0.27790
a_2	-0.14209	0.017900
a_3	0.032195	-0.0064649
a_4	-0.0017990	0

Polybutadiene has excellent resistance to low temperature brittleness^{311,362}. It also has excellent abrasion and flex-cracking resistance. The tensile strength of BR is lower than that of NR but can be improved through the use of carbon black loading. Polybutadienes are more permeable to gases than are NR or SBR but are similar in their resistance to oxidation and ozone. Polybutadienes also have a high volume resistivity.

Polybutadienes have fairly good resistance to acids and alkalies³¹¹. They have poor resistance to aliphatic and aromatic hydrocarbons and chlorinated solvents. They are fairly resistant to oxygenated solvents, such as ethers and esters, but have poor resistance to lubricating and hydraulic oils and fluids.

12.2 CHLOROSULFONATED POLYETHYLENE (HYPALON) (CSM)

Hypalon is the trade name of a chlorosulfonated polyethylene that is obtained by the treatment of low molecular weight polyethylene with chlorine and sulfur dioxide^{364,365}. There are four commercially available types (designated by Hypalon 20, 30, 40, and 45) that differ in their chlorine and sulfur contents. Hypalon is a very chemically stable material.

Cure of Hypalon is affected by heating with metal oxides in the presence of an organic acid. The primary curing agents for Hypalon are metallic oxides, organic compounds containing sulfur, and epoxy resins^{364,366}. Commercially used systems are litharge, litharge/magnesia, and magnesia/pentaerythritol. The cure mechanisms of hypalon are discussed in Refs. 364 and 365. The litharge/magnesia system provides very good heat resistance but does not have outstanding resistance to water and chemicals. Use of red lead improves water resistance.

Hypalon has superior ozone resistance, better than that of any other elastomer. It has excellent resistance to abrasion, weather, heat, flame, and crack growth. Hypalon also has low moisture absorption, good dielectric properties, and can be compounded in a variety of colors since it does not require carbon black for reinforcement. Hypalon has a

resistance to chemicals and oils that is similar to that of neoprene. It has excellent resistance to acids and oxidizing agents but poor resistance to gasoline, aromatic solvents, and chlorinated hydrocarbon solvents³¹¹.

Hypalon is used primarily in areas that require outstanding environmental resistance. Commercial applications include protective boots for spark plugs and electrical connectors, tank liners, and coated fabrics. It is a moderately expensive, special-purpose material that is not particularly recommended for dynamic applications.

12.3 STYRENE-BUTADIENE RUBBER (SBR)

Styrene-butadiene rubber is a general-purpose, non-oil resistant rubber manufactured by the copolymerization of butadiene and styrenes³⁶⁷. The temperature of the emulsion polymerization has an effect on the curing behavior and final properties of this elastomer. Gum stocks prepared at lower temperatures (the "cold" stocks) generally yield vulcanizates with higher tensile strengths, higher modulus, and better abrasion resistance than do "hot" stocks. Styrene-butadiene rubber is a relative inexpensive elastomer and is the most common synthetic elastomer in use today. It is widely used in tires, electrical products, toys, rollers, and in molded and extruded mechanical items.

Styrene-butadiene rubber can be cured by essentially the same cure systems as used for NR. Sulfur and sulfur donor systems are widely used.

Styrene-butadiene rubber must be reinforced to have acceptable tensile and tear strength for most applications³⁶⁴. Carbon black-filled compounds have lower densities, higher tensile strength, and lower water absorption than do mineral filled compounds. Styrene-butadiene rubber is less resilient than is NR and exhibits greater heat build up when flexed. Its low-temperature properties are also not as good as those of NR.

Styrene-butadiene rubber has fair-to-good weather, ozone, and oxidation resistance. Use of antioxidants is recommended. It has fair resistance to acids and alkalis. Styrene-butadiene rubber formulations tend to deteriorate after prolonged contact with oils and hydraulic fluids.

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APPENDIX 1 - GENERIC DESIGNATION CROSS INDEX

Generic Designation	Commercial or Trade Name	Manufacturer or Supplier
Acrylic (AM)	Cyanacril Hycar 4000 series Nipol series	American Cyanamid B.F. Goodrich Goldsmith & Eggleston
Butadiene (BR)	Cisdenes DIENE's (Buna CB's) Ameripol CB's Micro Black CB's Budene 1200 series JSR BR & RB series Solprene 233 TAKTENE Synpol E-BR series	American Synthetic Mobay Chem. Corp. B.F. Goodrich B.F. Goodrich Goodyear Tire JSR America Phillips Chemicals Polysar Intntl. Texas-U.S. Chemical
Chloroprene (CR)	Neoprene TW & WRP Neoprene E, M, or S Baypren series	E.I. DuPont Petro-Tex Chemical Mobay Chem. Corp.
Chlorosulfonated Polyethylenes (CSM)	Hypalon	E. I. DuPont
Epichlorohydrin (EC & ECO)	Gechron series Herchlor series Hydrin series	Goldsmith & Eggleston Hercules B.F. Goodrich
Ethylene-Propylene (EPM)	Epsyn 7006 Epcar 306 & 505	Copolymer Rubber B.F. Goodrich
Ethylene-Propylene-Diene (EPDM)	Epsyns except 7006 Nordels Epcars except 306 & 305 Royalenes	Copolymer Rubber E.I. DuPont B.F. Goodrich Uniroyal
Fluorocarbon (CFM)	Aflas Kalrez & Vitons Fluorels Technoflon	Xenox E.I. DuPont 3M Company Montedison, USA
Isobutylene	Vistanex	Exxon
Isobutylene Isoprene (IIR) [Butyl]	POLYSAR Butyls Bromobutyl series Exxon butyls Exxon chlorobutyls	Polysar Intntl. Exxon Exxon Exxon

(continued)

Elastomeric Materials for Acoustical Applications

GENERIC DESIGNATION CROSS INDEX (continues)

Generic Designation	Commercial or Trade Name	Manufacturer or Supplier
Isoprene (IR)	Ameripol SN's Natsyns DPR's TRANS-PIP's	B.F. Goodrich Goodyear Tire Hardman, Inc. Polysar Intntl.
Natural Rubber (NR)		
Nitrile (NBR)	Nysyn series Nysynhlak series Hycar 10XX & 14XX series Hycar Nitrile 1031, 1411, and 1432 series Chemigum N series KRYNAC series up to 810 and 843 Nipol series Paracril A, B, C, D, and J series Paracril 1880, 1880LM, 3300, and 4304 Perbunan	Copolymer Rubber Copolymer Rubber B.F. Goodrich B.F. Goodrich Goodyear Tire Polysar Intntl. Goldsmith & Eggleston Uniroyal Uniroyal Mobay Chem. Corp.
Polysulfides (T)	FA series LP series	Morton Thiokol/ Chemical Div. Morton Thiokol/ Chemical Div.
Polyurethanes (U)	Adiprenes Andur series Arcon series Calthane series Castathane series Castomer series CONAP series CONATHANE series Curene series Cyanaprene series Diosogrin series Multrathane PR Series Sorbothane Terathane Series	E.I. DuPont Anderson Dev. Co. Allied Resin Corp. Cal Polymers, Inc. Upjohn Co. Witco Chem. Co. Conap Inc. Conap Inc. Anderson Dev. Co. American Cyanamid Co. Diosogrin Indus. Corp. Mobay Chem. Corp. Products Res. & Chemical Co. Hamilton-Kent E. I. DuPont

(continued)

GENERIC DESIGNATION CROSS INDEX (continues)

Generic Designation	Commercial or Trade Name	Manufacturer or Supplier
Silicones (MQ)	G.E. Silicones	General Electric
	Rhodorsil series	Rhodia, Inc.
	Silastic series	Dow Corning
	SWS series	SWS Silicones Corp.
Styrene-Butadiene (SBR)	Ameripol	
	Numbered series	B.F. Goodrich
	ASRC series	American Synthetic
	Baytown series	Ashland Chemical Co.
	Carbomix series	Copolymer Rubber
	Cold Microblack series	B.F. Goodrich
	COPC series	Copolymer Rubber
	FR series	Firestone
	Kraton series	Shell Chem. Co.
	Krylene series	Polysar Intntl.
	Plioflex series	Goodyear Tire
	Synpol series	Texas-U.S. Chem. Co.

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APPENDIX 2 - COMMERCIAL NAME CROSS INDEX

Commercial or Trade Name	Generic Designation	Manufacturer or Supplier
Adiprenes	Polyurethane (U)	E.I. DuPont
Ameripol OB series	Butadiene (BR)	B.F. Goodrich
Ameripol SN series	Isoprene (IR)	B.F. Goodrich
Ameripol Numbered series	Styrene-Butadiene (SBR)	B.F. Goodrich
Andur series	Polyurethane (U)	Anderson Dev. Co.
Arcon series	Polyurethane (U)	Allied Resin Corp.
ASRO series	Styrene-Butadiene (SBR)	American Synthetic
Baytown series	Styrene-Butadiene (SBR)	Ashland Chemical Co.
BUOAR series	Isobutylene-Isoprene (IIR)	Cities Service Co.
Budene series	Butadiene (BR)	Gom Company
Calthane series	Polyurethane (U)	Cal Polymers Inc.
Carbonix series	Styrene-Butadiene (SBR)	Copolymer Rubber
Castathane series	Polyurethane (U)	Upjohn Company
Castomer series	Polyurethane (U)	Witco Chem. Co.
Catapol series	Polyurethane (U)	Arcco
Chemigum series	Nitrile (NBR)	Goodyear Tire
Cisdene	Butadiene (BR)	American Synthetic
Cold Microblack series	Styrene-Butadiene (SBR)	B.F. Goodrich
CONAP series	Polyurethane (U)	Conap Inc.
CONATHANE series	Polyurethane (U)	Conap Inc.
COPO series	Styrene-Butadiene (SBR)	Copolymer Rubber
Curene series	Polyurethane (U)	Anderson Dev. Co.
Cyanacryl series	Acrylic (AM)	American Cyanamid Co.

(continued)

COMMERCIAL NAME CROSS INDEX (continues)

Commercial or Trade Name	Generic Designation	Manufacturer or Supplier
Cyanaprene series	Polyurethane (U)	American Cyanamid Co.
DIENE series	Butadiene (BR)	Firestone
Diosogrin series	Polyurethane (U)	Diosogrin Indus. Corp.
DPR series	Isoprene (IR)	B.F. Goodrich
Duragen series	Butadiene (BR)	General Tire
Epcar series (except 306 & 505)	Ethylene-Propylene- Diene (EPDM)	B.F. Goodrich
Epcar 306 & 505	Ethylene-Propylene (EPR)	B.F. Goodrich
Epsyn series (except 7006)	Ethylene-propylene- Diene (EPDM)	Copolymer Rubber
Epsyn 7006	Ethylene-Propylene (EPR)	Copolymer Rubber
FA-3000 series	Polysulfide rubber (T)	Morton Thiokol/ Chemical Div.
Fluorel series	Fluorocarbon (CFM)	3M Company
FRS series	Styrene-Butadiene (SBR)	Firestone
G.E. Silicones	RTV Silicones	General Electric
Gentro series	Styrene-Butadiene (SBR)	General Tire
Hycar 4000 series	Acrylic (AM)	B.F. Goodrich
Hycar Nitriles	Nitrile (NBR)	B.F. Goodrich
Hypalon	Chlorosulfonated Poly- ethylene	E.I. DuPont
JSR BR & RB series	Butadiene (BR)	JSR Amer., Inc.
Kalrez series	Fluorocarbon (CFM)	E.I. DuPont
Kel-F series	Fluorocarbon (CFM)	3M Company
Kraton series	Styrene-Butadiene (SBR)	Shell Chem. Co.
Krylene series	Styrene-Butadiene (SBR)	Polysar Intntl.

(continued)

COMMERCIAL NAME CROSS INDEX (continues)

Commercial or Trade Name	Generic Designati.	Manufacturer or Supplier
LP series	Polysulfide rubber (T)	Morton-Thiokol/ Chemical Div.
Multrathane F series	Polyurethane (U)	Mobay Chem. Corp.
Neoprene series	Polychloroprene	E.I. DuPont
Nordel series	Ethylene-Propylene- Diene (EPDM)	E.I. DuPont
Nysyn series	Nitrile (NBR)	Copolymer Rubber
Nysyn Blak series	Nitrile (NBR)	Copolymer Rubber
Paracril series	Nitrile (NBR)	Uniroyal
Plioflex series	Styrene-Butadiene (SBR)	Goodyear Tire
POLYSAR Butyls	Isobutylene-Isoprene (IIR)	Polysar Intntl.
PR series	Polyurethane (U)	Products Research & Chemicals
Rhodorsil series	Silicone (MO)	Rhodia, Inc.
Royalene series	Ethylene-Propylene- Diene (EPDM)	Uniroyal
Silastic series	Silicone (MO)	Dow Corning
Solprene 233	Butadiene (BR)	Phillips Chemicals
Sorbothane	Polyurethane (U)	Hamilton-Kent
SWS series	Silicone (MO)	SWS Silicones Corp.
Synpol E-BR series	Butadiene (BR)	Texas-U.S. Chem. Co.
TAKTENE	Butadiene (BR)	Polysar Intntl.
Vibrathane	Polyurethane (U)	Uniroyal
Viton	Fluorocarbon (CFM)	E.I. DuPont

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APPENDIX 3 - MANUFACTURERS OR SUPPLIERS INDEX

AGI Rubber Co.
135-A Stratford Avenue
Bridgeport, CT 06608
(203) 366-4318

American Cyanamid Co.
Bound Brook, NJ 08805
(201) 356-2000

Anderson Development Co.
1415 E. Michigan Street
Adrian, MI 49221
(517) 263-2121

Ashland Chemical Co.
P.O. Box 2219
Columbus, OH 43216
(614) 889-3333

Buckeye Rubber Products
777 Benra Street
Lima, OH 45802
(419) 228-4441

Cal Polymers Inc.
2115 Gaylord St.
Long Beach, CA 90813
(213) 436-7372

Conap Inc.
1405 Buffalo Street
Olean, NY 14760
(716) 372-9650

Diosogrin Industries Corp.
Grenier Field
Manchester, NH 03103
(603) 669-4050

Dow Corning Corp.
Midland, MI 48640
(517) 496-4000

Emerson and Cuming Inc.
869 Washington Street
Canton, MA 02021

Garrett Flexible Products Inc.
1101 S. Cowen Street
Garrett, IN
(219) 357-4133

Allied Resin Corp.
Weymouth Industrial Park
East Weymouth, MA 02189
(617) 337-6070

American Synthetic Rubber Co.
P.O. Box 360
Louisville, KY 40201
(504) 448-2761

Arnco
4676 Admiralty Way
Marina Del Rey, CA 90291
(213) 822-5282

BASF Wyandotte Corp.
Wyandotte, MI 48192
(313) 292-3300

Burke Rubber Co.
2250 S. 10th St. at Burke
San Jose, CA 95112
(408) 297-3500

Cities Service Co.
Columbian Division
3200 W. Market St.
Fairlawn Village
Akron, OH 44313
(216) 867-5800

Copolymer Rubber and Chemical Co.
P.O. Box 2591
Baton Rouge, LA 70821
1-800-535-9960

E.I. DuPont de Nemours and Co.
1007 Market Street
Wilmington, DE 19898
(302) 774-2421

Exxon Chem. Co.
P.O. Box 3272
Houston, TX 77001

Firestone Synthetic Rubber & Latex Co.
1200 Parkstone Pkwy.
Akron, OH 44317
(216) 379-7000

(continued)

MANUFACTURERS OR SUPPLIERS INDEX (continues)

General Electric
Silicone Products Department
Waterford, NY 12188
(518) 237-3330

B.F. Goodrich Chemical Co.
8100 Oak Blvd.
Cleveland, OH 44131
(216) 794-2121

Hamilton-Kent
Box 178
Kent, OH 44240
(216) 524-0200
or 800-321-2188

Hexcel Corporation
Resin Chemicals Group
20701 Nordhoff Street
Chatsworth, CA 91311
(213) 882-3022

Jacobs Rubber Co.
101 Lake Rd.
Dayville, OR 97241
(203) 774-9611

Karmon Rubber Co.
2333 Copley Road
Akron, OH 44320
(216) 864-2161

Master Processing Corp.
2502 Thompson Street
Long Beach, CA 90805
(213) 531-3880

Montedison USA, Inc.
1114 Ave. of The Americas
New York, NY 10036
(212) 764-0275

Paramount Packing & Rubber, Inc.
4018 Belle Grove Road
Baltimore, MD 21225
(301) 789-2236

General Tire & Rubber Co.
1 General Street
Akron, OH 44329
(216) 789-3000

Goodyear Tire & Rubber Co.
Rubber Division
P.O. Box 9023
Akron, OH 44305

Hardman, Inc.
Belleville, NJ 17109
(201) 751-3000

Huntington Rubber Co.
P.O. Box 570
Portland, OR 97207
(503) 246-5411

Isochem Resins
99 Cook Street
Lincoln, RI 02865
(401) 723-2100

JSR America, Inc.
350 Fifth Avenue
Suite 8001
New York, NY 10001

Kirkhill Rubber Co.
Cypress Court
Brea, CA 92611
(714) 529-4901

Mobay Chemical Corp.
Polyurethane Division
Pittsburgh, PA 15205
(412) 923-2700

Morton Thiokol/Chem. Div.
101 Carnegie Center
Princeton, NJ 08540
(609) 396-4001

Pawling Rubber Corp.
157-A Maple Blvd.
Pawling, NY 12564
(914) 855-1000

(continued)

MANUFACTURERS OR SUPPLIERS INDEX (continues)

Petro-Tex Chemical Co.
8600 Park Place Blvd.
Houston, TX 77017
(713) 477-9211

Polysar International
1795 West Market Street
Akron, OH 44313
(262) 836-0451

Products Res. & Chem. Corp.
5454 San Fernando Road
P.O. Box 1800
Glendale, CA 92108
(213) 240-2060

Rubber Corporation of America
2535 N. Broad Street
Philadelphia, PA 19132
(215) 225-3700

Salem Republic Rubber Co.
California & 19th Street
Sebring, OH 44672
(216) 938-9001

Smithers Scientific Services
421 West Market Street
Akron, OH 44303
(216) 762-7441

SWS Silicones Corp.
Div. of Stauffer Chem. Co.
Adrian, MI 49221
(517) 263-5711

Texas-U.S. Chemical Co.
One Greenwich Plaza
Greenwich, CT 06830
(203) 661-3050

Unirubber, Inc.
130-A East 35 Street
New York, NY 10016
(212) 685-0200

William-Bowman Rubber Co.
1945 S. 54th Avenue
Cicero, IL 60650
(312) 242-1640

Pelmor Laboratories, Inc.
400 Lafayette Street
Newton, PA 18940
(214) 968-3825

Phillips Chemicals
Division of Phillips Petroleum Co.
International Department
1501 Commerce Drive
Stow, OH 44224
(216) 688-6652

Precision Associates, Inc.
742 N. Washington Avenue
Minneapolis, MN 55401
(612) 336-8394

Rhodia, Inc.
P.O. Box 125
Monmouth Junction, NJ 08852
(201) 877-7700

Rubber Crafters, Inc.
P.O. Box 356
South Plainfield, NJ 07080
(201) 754-8100

Shell Chemical Co.
One Shell Plaza
Houston, TX 77002
(713) 220-6161

Star-Glo Industries, Inc.
4 Carlton Avenue
East Rutherford, NJ 07073
(201) 939-6162

Uniroyal Chemicals Division
Division of Uniroyal, Inc.
Elm Street
Naugatuck, CT 06770
(203) 723-3000

Upjohn Company
OPR Division
555 Alaska Avenue
Torrence, CA 90503
(213) 320-3550

(continued)

MANUFACTURERS OR SUPPLIERS INDEX (continues)

Witco Chemical Co.
Organic Division
400 N. Michigan Avenue
Chicago, IL 60611
(312) 644-7200

3M Company
Commercial Chemicals Div.
3M Center
St. Paul, MN 55101
(612) 733-1110

APPENDIX 4 - MANUFACTURERS OF ADHESIVES

Adchem Corporation
625 Main Street
Westbury, NY 11590
(516) 333-3843

Adhesives Research, Inc.
161 E. Ninth Avenue
York, PA 17404
(717) 235-4860

Allaco Products
130 Wood Road
Braintree, MA 02184
(617) 928-2550

Allied Adhesive Corp.
91-20-130th Street
Richmond Hill, NY 11418
(212) 846-3200

American Metaseal Co.
509 Washington Avenue
Carlstadt, NJ 07072
(201) 933-1720

Argo Paint and Chemical Co.
19440 Fitzpatrick Street
Detroit, MI 48228
(313) 729-7400

Atlantic Paste & Glue Co.
9 53rd Street
Brooklyn, NY 11232
(212) 492-3648

BFC Division
Essex Chemical Corporation
1401 Broad Street
Clifton, NJ 07012
(201) 773-6300

Baltimore Adhesive Co.
Reisterstown Road
Cummings Mills, MD 21117
(301) 363-0177

Bay State Adhesive Corp.
South Mason Street
Salem, MA 01970
(617) 744-8237

Adhesive Products, Inc.
520 Cleveland Avenue
Albany, CA 94710
(212) 542-4600

Alco Chemical Corp.
Trenton Avenue & Williams St.
Philadelphia, PA 19134
(215) 425-0621

Allen Products Corp.
9214 Livernois Avenue
Detroit, MI 48204
(313) 924-7400

American Cyanamid Co.
Ind. Chemical Div.
Berdan Avenue
Wayne, NJ 07470
(201) 831-1234

Applied Plastics Co., Inc.
130 Penn Street
El Segundo, CA 90245
(213) 322-8050

Armstrong Products Co., Inc.
Argonne Road
Warsaw, IN 46580
(219) 267-3228

Atlas Minerals & Chemicals Div.
ESB, Inc.
Mertztown, PA 19539
(215) 682-7171

Baker Sealants & Coatings Co.
234 Suydam Avenue
Jersey City, NJ 07304
(201) 333-6986

Barker Chemical Co.
700 E. 138th Street
Chicago, IL 60627
(312) 995-9600

Berco Industries Corp.
1250 Shames Drive
Westbury, NY 11590
(516) 334-4222

(continued)

MANUFACTURERS OF ADHESIVES (continues)

Bond Adhesives Co.
120 Johnston Avenue
Jersey City, NJ 07303
(201) 243-8100

Calopolymers, Inc.
2115 Gaylord Street
Long Beach, CA 90813
(213) 436-7372

Carboline Co.
328 Hanley Ind. Court
St. Louis, MO 63144
(314) 644-1000

Cementex Co., Inc.
336 Canal Street
New York, NY 10013
(212) 226-5832

Chemical Coatings & Eng. Co.
221 Brooks Street
Media, PA 19063
(215) 566-7470

Chicago Adhesive Products Co.
4658 W. 60th Street
Chicago, IL 60629
(312) 581-1300

Clifton Adhesive, Inc.
Burgess Place
Wayne, NJ 07470
(201) 894-0845

Conap, Inc.
184 E. Union Street
Allegheny, NY 14708
(716) 372-9650

Conwed Corp.
2200 Highcrest Street
St. Paul, MN 55113
(612) 221-1100

DAP, Inc.
5300 Huberville Road
Dayton, OH 45431
(513) 253-7151

Burrage Glue Co.
91-20 130th Street
Richmond Hill, NY 11418
(212) 846-1600

Can-Tite Rubber Corp.
33 Redfern Avenue
Inwood, NY 11696
(212) 327-2800

Cat's Paw Rubber Co.
Warner & Ostend Streets
Baltimore, MD 21230
(617) 884-1700

Chemical Seal Corp. of America
598 West Avenue 26
Los Angeles, CA 90065
(213) 982-1655

Chemical Sealing Corp.
5401 Banks Avenue
Kansas City, MO 64130
(816) 923-8812

Chrysler Corporation
Chemical Division
5437 Jefferson Street
Trenton, MI 48183
(312) 956-5741

Commercial Chemical Co.
1021 Summer Street
Cincinnati, OH 45204
(513) 921-8600

Contact Industries, Inc.
850 S. Oyster Bay Road
Hicksville, NY 11801
(201) 251-5900

Peter Cooper Corp.
Palmer Street
Gowanda, NY 14070
(716) 532-3344

Dow Corning Corp.
Midland, MI 48640
(517) 496-4000

(continued)

MANUFACTURERS OF ADHESIVES (continued)

E.I. DuPont de Nemours & Co.
1007 Market Street
Wilmington, DE 19898
(302) 774-2421

Fel-Pro, Inc.
7450 N. McCormick Blvd.
Skokie, IL 60076
(312) 874-7700

Firestone Tire and Rubber Co.
1200 Firestone Parkway
Akron, OH 44317
(216) 379-7000

Benjamin Foster Div.
Amchem Products, Inc.
Brookside Avenue
Ambler, PA 19002
(215) 628-7000

Gates Eng. Div., SCM Corp.
100 S. West Street
Wilmington, DE 19899
(302) 656-9951

Gilsonite Co.
2946 Northeast Columbia Blvd.
Portland, OR 97211
(503) 288-5454

Goodyear Tire & Rubber Co.
Chemical Division
1485 E. Archwood Avenue
Akron, OH 44318
(216) 794-3010

Hughson Chemical Co.
2000 W. Grandview Blvd.
Erie, PA 16509
(313) 588-1500

Imperial Adhesives & Chem., Inc.
6315 Wiehe Road
Cincinnati, OH 45237
(513) 841-4545

Isochem Resins Co.
99 Cook Street
Lincoln, RI 02865
(401) 723-2100

Epoxylite Corp.
1901 Via Burton
Anaheim, CA 92806
(714) 830-7910

Findley Adhesives, Inc.
3033 W. Pemberton Avenue
Milwaukee, WI 53245
(414) 782-2250

Flexcraft Industries, Inc.
527 Avenue P
Newark, NJ 07105
(201) 589-3403

Franklin Glue Co.
2020 Beuck Street
Columbus, OH 43207
(614) 443-0241

General Adhesives & Chem. Co.
8100 Centennial Blvd.
Nashville, TN 37209
(615) 367-6833

B.F. Goodrich Ind. Prod. Co.
Adhesive Prod. Div.
500 S. Main Street
Akron, OH 44318
(216) 379-2000

Holt Mfg. Co., Inc.
2615 Fifth Avenue S.
Birmingham, AL 35233
(205) 956-3789

ICI America, Inc.
151 South Street
Stamford, CT 06904
(302) 575-3000

Industrial Polychemical Service
17116 S. Broadway
Gardena, CA 90247
(213) 321-6515

Jones Chemical Co.
1230 Harry Hines Blvd.
Dallas, TX 75234
(214) 861-5425

(continued)

MANUFACTURERS OF ADHESIVES (continues)

Key Polymer Corp.
275 Lowell Street
Lawrence, MA 01842
(617) 683-9411

Loctite Corp.
705 N. Mountain Road
Newington, CT 06111
(800) 243-8810

Narmco Materials Div.
Whittaker Corp.
600 Victoria Street
Costa Mesa, CA 92627
(714) 548-1144

Ohio Sealer Div.
NDW Corporation
3040 East River Road
Dayton, OH 45439
(513) 294-1767

Pemco Adhesives, Inc.
West Township Road
Auburn, IN 46706
(219) 925-3368

Pilot Chemical Co., Inc.
10-30 Jackson Avenue
Long Island City, NY 11101
(212) 729-8282

Presto Adhesives, Inc.
5436 W. Rogers Street
West Allis, WI 53219[B
(414) 327-3450

Radioptics, Inc.
10 Dupont Street
Plainview, NY 11803
(516) 935-3050

Research Sales, Inc.
Route 202 & Ramapo Avenue
Mahwah, NJ 07430
(201) 529-3676

Patrick Ross Co.
619 Somerville Avenue
Somerville, MA 02141
(617) 354-8100

H.B. Fred Kuhls Co.
49 Summer Street
Milford, MA 01757
(617) 473-3424

Minnesota Mining & Mfg. Co. (3M)
3M Center
St. Paul, MN 55101
(612) 733-1110

National Starch & Chem. Corp.
750 Third Street
New York, NY 10017
(201) 885-5000

PPG Industries
225 Belleville Avenue
Bloomfield, NJ 07003
(412) 434-3131

Pierce & Stevens Chem. Corp.
710 Ohio Street
Buffalo, NY 14203
(716) 856-4910

Polymer Chemical Co.
131 Barron Drive
Cincinnati, OH 45215
(513) 771-6324

Products Research & Chem. Corp.
2919 Empire Avenue
Burbank, CA 91504
(213) 240-2060

Raybestos-Manhattan, Inc.
75 E. Main Street
Stratford, CT 06601
(203) 371-0101

Roberts Consolidated Ind., Inc.
600 E. Evergreen Road
Monrovia, CA 91016
(212) 422-4170

Rubba, Inc.
1015 E. 173rd Street
Bronx, NY 10460
(212) 542-4661

(continued)

MANUFACTURERS OF ADHESIVES (continues)

Rubber Latex Co. of America
210 Delawanna Avenue
Clifton, NJ 07014
(201) 473-3020

Service Adhesives Co., Inc.
1214 S. 6th Street
Maywood, IL 60153
(312) 681-5751

Smooth-On, Inc.
1000 Valley Road
Gillette, NJ 07933
(201) 647-5800

Sta-Bond Corp.
14101 S. Western Avenue
Gardena, CA 90249
(213) 770-0591

Standard Paste & Glue Co.
3824 W. 38th Street
Chicago, IL 60632
(312) 523-1412

Testworth Laboratories, Inc.
139 Commercial Road
Addison, IL 60101
(219) 244-5137

USM Corp., Chemical Div.
Middleton, MA 01949
(617) 777-0100

Uniroyal Chemical Div.
Uniroyal, Inc.
Elm Street
Naugatuck, CT 06770
(203) 723-3000

United Resin Products, Inc.
100 Sutton Street
Brooklyn, NY 11222
(212) 384-3000

U.S. Gypsum Co.
101 S. Wacker Drive
Chicago, IL 60606
(312) 321-4000

Ruco Div. Hooker Chemical Co.
New South Road
Ricksville, NY 11082
(609) 499-2300

Shuford Mills, Inc.
Highland Avenue & 15th Street
Hickory, NC 28601
(704) 322-2700

Southern Adhesives Corp.
4105 Castlewood Road
Richmond, VA 23234
(513) 561-8440

Sta-Crete, Inc.
893 Folsom Street
San Francisco, CA 94107
(213) 868-6511

Sullivan Chemicals Div.
Sullivan Varnish Co.
420 N. Hart Street
Chicago, IL 60622
(312) 666-8080

Thiokol Chemical Corp.
930 Lower Ferry Road
Trenton, NJ 08607
(609) 396-4001

Uniroyal, Inc.
Adhesives & Coatings Dept.
312 North Hill
Mishawaka, IN 46544
(219) 255-2181

Uniseal, Inc.
1181 Diamond Avenue
Evansville, IN 47711
(812) 425-1361

U.S. Adhesives Co.
1735 W. Carroll Avenue
Chicago, IL 60612
(312) 829-7438

Virginia Adhesives Corp.
1920 Rose Lane
Lynchburg, VA 24505
(804) 846-1466

(continued)

Elastomeric Materials for Acoustical Applications

MANUFACTURERS OF ADHESIVES (continues)

West Chester Chem. Co.
439 S. Bolar Street
West Chester, PA 19380
(215) 696-9220

Williamson Adhesives, Inc.
8220 Kimball Avenue
Skokie, IL 60076
(312) 673-6890

Whittaker Corp.
10 S. Electric Street
P.O. Box 27
West Alexandria, OH 45381
(513) 839-4612
(513) 835-5656

APPENDIX 5 - TRANSDUCER FILL FLUIDS

A5.1 GENERAL INFORMATION

Dielectric fluids are used in underwater acoustics as coupling media both in laboratory measurement systems and sonar transduction devices³⁶⁸. The latter category is of more practical importance for purposes of this work, since many sonar transducers require a coupling medium to transmit sound waves from the active element to water. Reciprocal transducers that act as receivers usually also require the use of liquid coupling media to couple sound into the receiving element from the water.

The properties that a liquid should possess to be acceptable as a sound transfer medium in transducer applications have been discussed by Green³⁶⁸ and Del Grosso and Smura³⁶⁹. These properties can be grouped into four broad categories: (1) acoustical, (2) physical, (3) chemical, and (4) environmental.

The acoustical properties that are generally desired are a close match in acoustic velocity and impedance to seawater to prevent diffraction losses and reflections at transducer windows. Attenuation per unit path length of the liquid may also be a significant factor at higher frequencies, although the effect may be minimized by using a thin layer of the coupling material. The fluid should also have a high cavitation threshold.

The physical properties that an ideal acoustic transfer fluid should possess are: moderate viscosity (for ease of filling) and low pour or freezing point, high flash point, density slightly greater than water (except for cases such as towed arrays where neutral or positive buoyancy is desirable), high thermal conductivity and low coefficient of thermal expansion, low water solubility, relatively high surface tension and adequate lubrication properties, and low electrical conductivity and high dielectric strength even when seawater solutions or emulsions are formed³⁷⁰. It should also possess a low vapor pressure to allow for ease of degassing and for safety considerations in its use.

The fill fluid itself should have long-term chemical stability with resistance to hydrolysis, polymerization, or oxidative breakdown. It should also be chemically inert toward encapsulant or transducer window materials.

The acoustic coupling fluid should be non-toxic and non-irritating. As mentioned earlier, it should have a low vapor pressure. It should also be relatively amenable to easy cleanup and safe disposal. Additionally, it should be readily available and relatively inexpensive.

These categories of properties are not listed in any order of importance, since each individual application will influence the role of these functions in the final selection of a fluid. Also, some of these desired properties are in opposition. Unlike water, the fluids will have a negative temperature coefficient of velocity. A high cavitation threshold and moderate viscosity are difficult to achieve simultaneously since the two are interdependent. If the density and sound velocity requirements are both met, the resultant acoustic impedance will be higher than that of water. Many of the liquids that have been considered for use as fill fluids also tend to permeate rubbery polymers, acting as plasticizers on these materials. They may also cause extreme chemical degradation in some cases, causing failure of the transducer window material. In general, swelling, chemical reaction between the polymer and solvent, and permeation of the solvent through the polymer may take place. It is possible (and usually probable) that all of these will occur simultaneously.

The permeation of many polymers by liquids takes place by a mechanism of activated diffusion³⁷¹⁻³⁷³. This is a 3-step process. The first step involves absorption of the permeating molecule at its ingoing surface and dissolving of the molecule into the polymer. The rate of solution will be governed by the vapor pressure of the permeant on the high-pressure side of the polymer barrier.

The second step is diffusion of the permeating molecule within the polymer membrane. Diffusion will occur with and against the direction of flow but is greater in the direction of flow. Factors affecting the rate of diffusion are the concentration gradient within the polymer, activation

energy for the process, and temperature. The concentration gradient is responsible for diffusion primarily in the direction of flow because the probability of a given molecule moving will be proportional to the concentration at the site of the molecule³⁷¹⁻³⁷³. The activation energy is the energy needed to separate polymer chains and permit passage of the migrating molecule. The percentage of molecules with the necessary energy is determined by the temperature.

Desorption of the migrating molecule is the third and final step in this process. The rate of desorption will be determined by the vapor pressure at the outgoing surface, which also influences the rate of permeation by determining the concentration gradient within the polymer membrane.

Hydrostatic pressure appears to have only a very small effect on the permeation rate for polymers where the mechanism is one of activated diffusion³⁷³, except in those cases where phenomena such as pressure-induced crystallization occur. The force exerted by the hydrostatic pressure is too small to cause movement of molecules through the polymer. The probability of the molecule having sufficient energy to form a hole between the polymer chains determines whether or not it will move. The concentration gradient determines whether or not it will move in the right direction. This, in turn, is determined by the vapor pressure differential on the two sides of the membrane. A detailed thermodynamic argument has been given by Lebovits³⁷³ to show that the vapor pressure determines the concentration of the permeant within the membrane. Additional complications (such as permeants that swell the membrane, second-order transition points in the polymer, or two membranes in series) are treated in Ref. 371.

The rate of permeation through the barrier will be influenced by various aspects of the material. These include the chemical composition of the polymer, chemical similarities between the polymer and the permeant, degree of crosslinking, type and amount of any fillers, crystallinity of the polymer, degree of plasticization by a foreign plasticizer (or the permeant itself), and sometimes by the previous history of the polymer^{371,374}. For a more complete discussion of polymer permeability (as

well as test procedures for evaluating water absorption, water vapor transmission, and effects of fluids on polymers), it is recommended that the reader consult Refs. 371 through 377, as well as ASTM's D471, D814, D1460, and D3137.

Acoustical data for a variety of fluids have been tabulated in Refs. 378 through 382. These data may prove to be useful to those concerned with relations between molecular parameters and acoustic propagation in these materials. We shall not reproduce these data here, but instead will concern ourselves only with a relatively few dielectric fluids that have found applications in sonar systems. None of these materials are considered suitable for sewer disposal, and care should be taken in their ultimate disposition. The recommended mode of disposal is incineration by a licensed disposal firm.

A5.2 CASTOR OIL

Castor oil has been, and is being, widely used as a fill fluid for sonar transducers. Two varieties are commonly used. These are DB grade and Lubricin castor oil.

DB grade (Vi-Chem, Miami, FL) is currently used in standard transducers at USRD. It is primarily a tri-ester of ricinoleic acid and glycerol, with an average molecular weight of 928 grams/mole. DB grade is used primarily because its acoustic properties are a relatively close match to those of seawater. Its longitudinal wave velocity, as determined by Green³⁶⁶, is depicted graphically in Fig. A5.1 as a function of temperature, while its acoustic impedance is shown in Fig. A5.2. Timme³⁷⁶ has expressed the pressure and temperature dependence of the sound speed in this material in the functional form

$$C = 1570(1.000 - 2.15 \times 10^{-3}T + 4.0 \times 10^{-6}T^2 + 2.5 \times 10^{-6}TP + 2.22 \times 10^{-3}P - 3.0 \times 10^{-6}P^2),$$

where C is in m/sec, T is in $^{\circ}\text{C}$, and P is hydrostatic pressure in MPa. Moffett³⁸³ obtained a cavitation threshold value of 233 dB/re $1\mu\text{Pa}$ for this material.

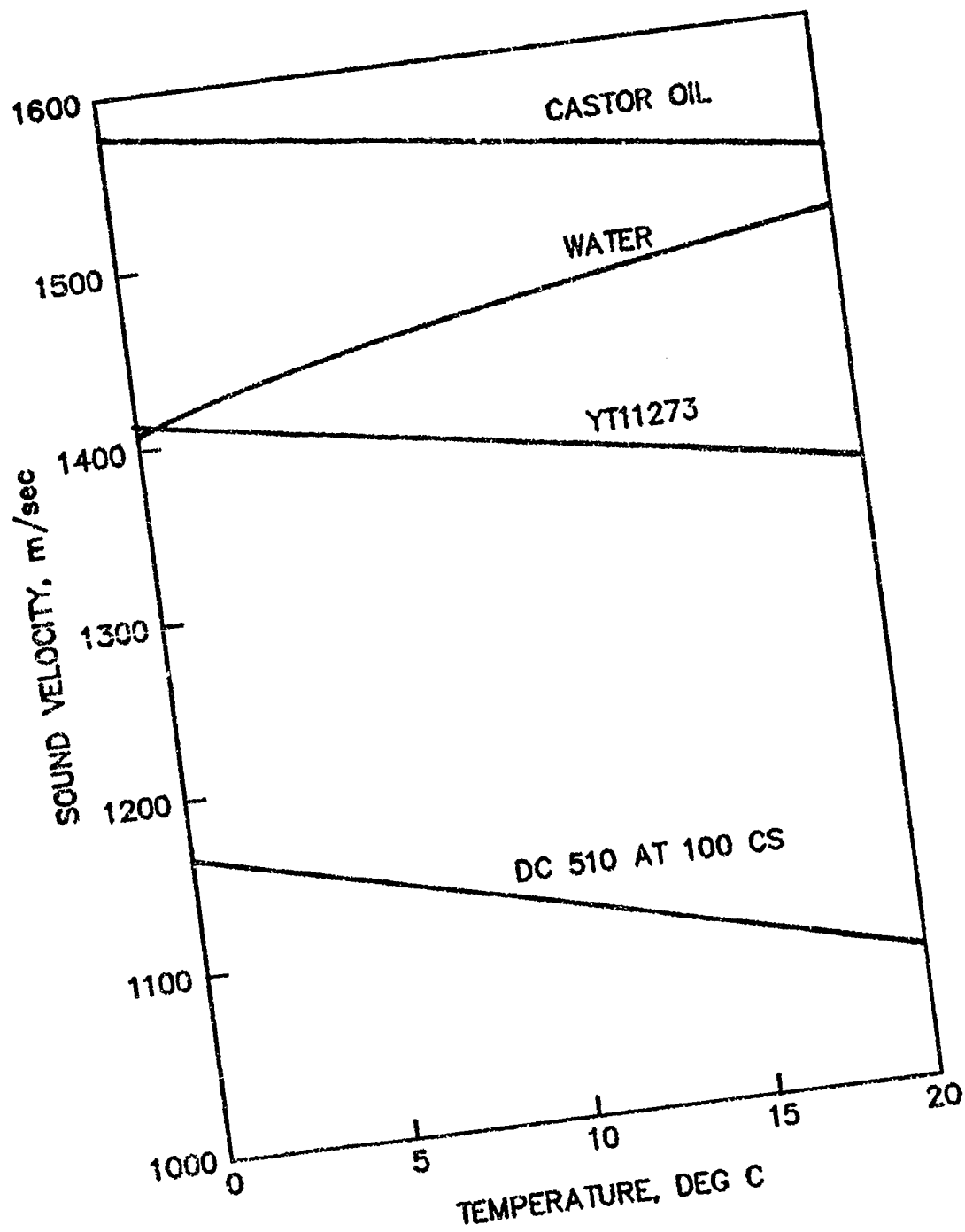


Fig. A5.1 - Velocity of sound as a function of temperature

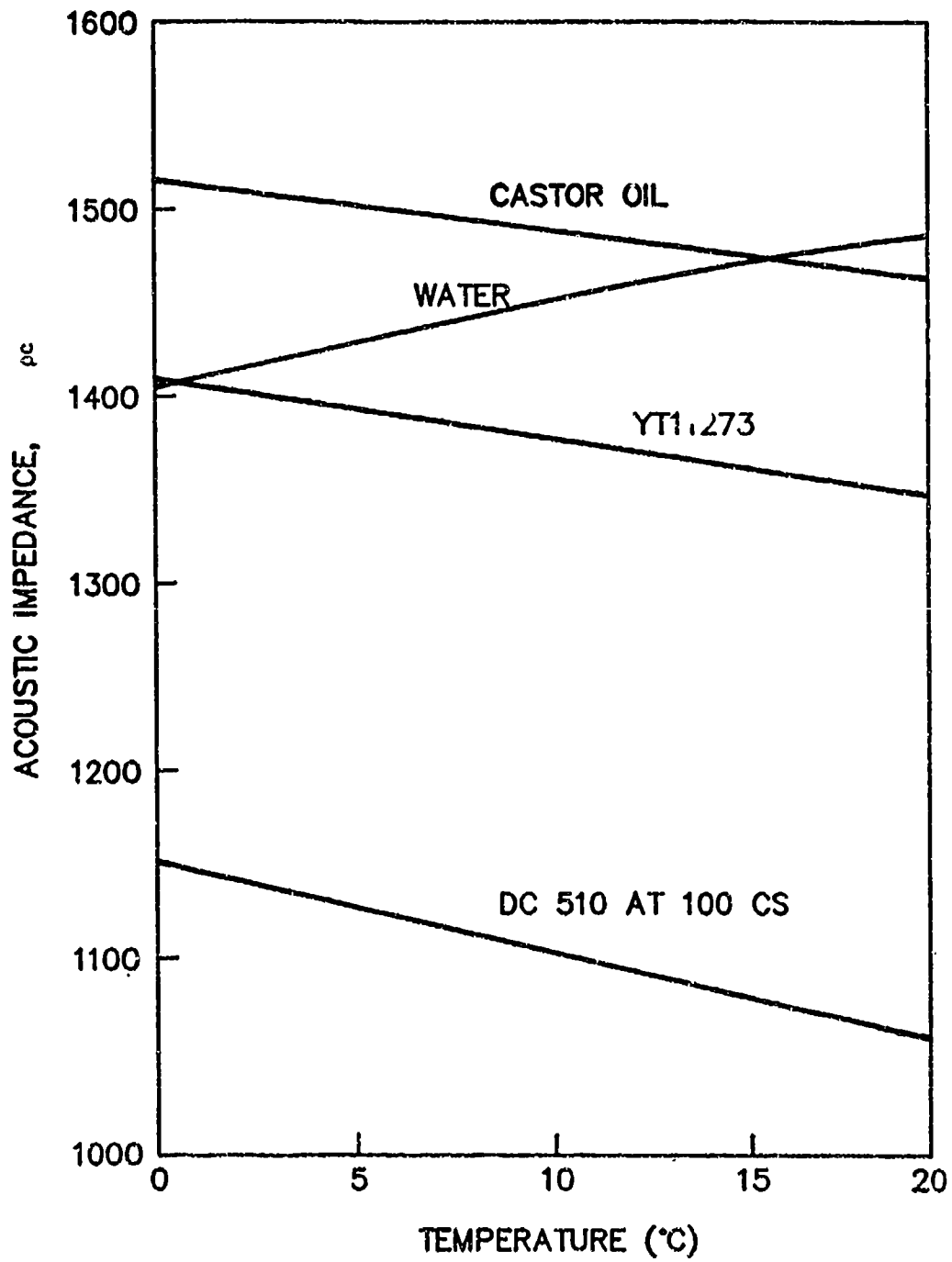


Fig. A5.2 - Acoustic impedance as a function of temperature

Stollard³⁸⁴ measured the specific volume, isothermal compressibility, and coefficient of thermal expansion in this material as a function of both temperature and pressure. The specific volume obtained by Stollard as a function of temperature and pressure is given in Fig. A5.3. Values of the isothermal compressibility and coefficient of thermal expansion are given in Tables A5.1 and A5.2. Timme³⁸⁵ obtained a polynomial function for the behavior of the density with pressure and temperature of the form

$$\rho = 1000 / (1.02714 + 7.04 \times 10^{-4} T + 9.66 \times 10^{-7} T^2 + 3.0 \times 10^{-9} T^3 - 4.91 \times 10^{-4} P - 2.633 \times 10^{-5} PT - 4.04 \times 10^{-9} PT^2 - 8.8 \times 10^{-11} PT^3 + 1.471 \times 10^{-6} P^2 + 9.2 \times 10^{-9} P^2 T + 3.6 \times 10^{-11} P^2 T^2 - 3.63 \times 10^{-9} P^3 - 1.66 \times 10^{-11} P^3 T),$$

where ρ is in kg/m³, T is in °C, and P is in MPa.

Other documented physical properties of this material include a volume electrical resistivity³⁸⁶ of 6×10^{10} ohm·cm and a surface tension³⁸⁰ of 0.06736 N/m. Its water solubility limit has been determined to be 1.4% at 25°C (Ref. 387).

One of the primary disadvantages of DB grade castor oil is its relatively high viscosity at low temperatures. Results of measurements of the viscosity as a function of temperature by Green are shown in Fig. A5.4. Timme³⁸⁶ obtained a value of 725 centipoise at 25°C, still a relatively high value at this temperature.

Castor oil has good to excellent compatibility with butyl and chlorobutyl rubber, including the H862A formulation given in Ch. 5 of this work. It is also compatible with neoprene formulations, as well as the EPDM-RLE formulation listed Ch. 6. It is compatible with Adiprene L100 and L315³⁸⁷. It has fair long-term compatibility with PR 1592³⁵⁹ and Goodrich castable Rho-C. DB grade castor oil has poor compatibility with PR 1574, EN 5, and EN 9. It is also reported to have poor compatibility with DC100, DC116; and NC775 cork-rubber composites³⁸⁸. It has fair compatibility with NC 710 and excellent compatibility with LC800. It is also compatible with polycarbonate and syntactic foam.

TABLE A5.1 - COMPRESSIBILITY OF BAKER DB-GRADE CASTOR OIL[†]

MPa											
T (°C)	0.1	10	20	30	40	50	60	70	80	90	100
0	+47.8	+45.2	+42.9	+40.7	+38.7	+36.9	+35.3	+33.9	+32.7	+31.7	+30.9
5	48.9	46.3	43.9	41.6	39.6	37.7	36.0	34.6	33.3	32.3	31.5
10	50.0	47.4	44.9	42.5	40.4	38.5	36.8	35.3	34.0	32.9	32.0
15	51.2	48.5	45.9	43.5	41.3	39.3	37.5	36.0	34.6	33.5	32.6
20	52.4	49.6	46.9	44.5	42.2	40.2	38.3	36.7	35.3	34.1	33.1
25	53.6	50.7	48.0	45.5	43.1	41.0	39.1	37.4	35.9	34.7	33.7
30	54.9	51.9	49.1	46.5	44.1	41.9	39.9	38.1	36.6	35.3	34.2
35	56.2	53.1	50.2	47.5	45.1	42.8	40.7	38.9	37.3	35.9	34.8
40	57.5	54.4	51.4	48.7	46.1	43.8	41.6	39.7	38.1	36.6	35.4

†From Ref. 384

(Units of compressibility (10⁻⁶ MPa⁻¹))

[†]From Ref. 384(Units of compressibility (10^{-6} MPa⁻¹))

TABLE A5.2 - THERMAL EXPANSION OF BAIRR DB-GRADE CASTOR OIL[†]

T (°C)	0.1	10	20	30	40	50	60	70	80	90	100
0	+6.85	+6.64	+6.43	+6.24	+6.06	+5.90	+5.74	+5.60	+5.46	+5.33	+5.21
5	6.92	6.71	6.50	6.31	6.13	5.96	5.81	5.66	5.53	5.40	5.30
10	7.00	6.78	6.57	6.38	6.19	6.03	5.87	5.73	5.59	5.47	5.35
15	7.08	6.85	6.64	6.44	6.26	6.09	5.93	5.78	5.65	5.52	5.41
20	7.16	6.93	6.71	6.51	6.32	6.15	5.98	5.83	5.70	5.57	5.46
25	7.25	7.01	6.78	6.58	6.38	6.20	6.03	5.88	5.74	5.61	5.50
30	7.34	7.09	6.86	6.64	6.44	6.25	6.08	5.92	5.78	5.65	5.53
35	7.43	7.17	6.93	6.71	6.50	6.30	6.13	5.96	5.81	5.67	5.55
40	7.52	7.26	7.01	6.77	6.56	6.35	6.17	5.99	5.83	5.69	5.56

[†]From Ref. 384(Units of thermal expansion: °C⁻¹ × 10⁻⁴)

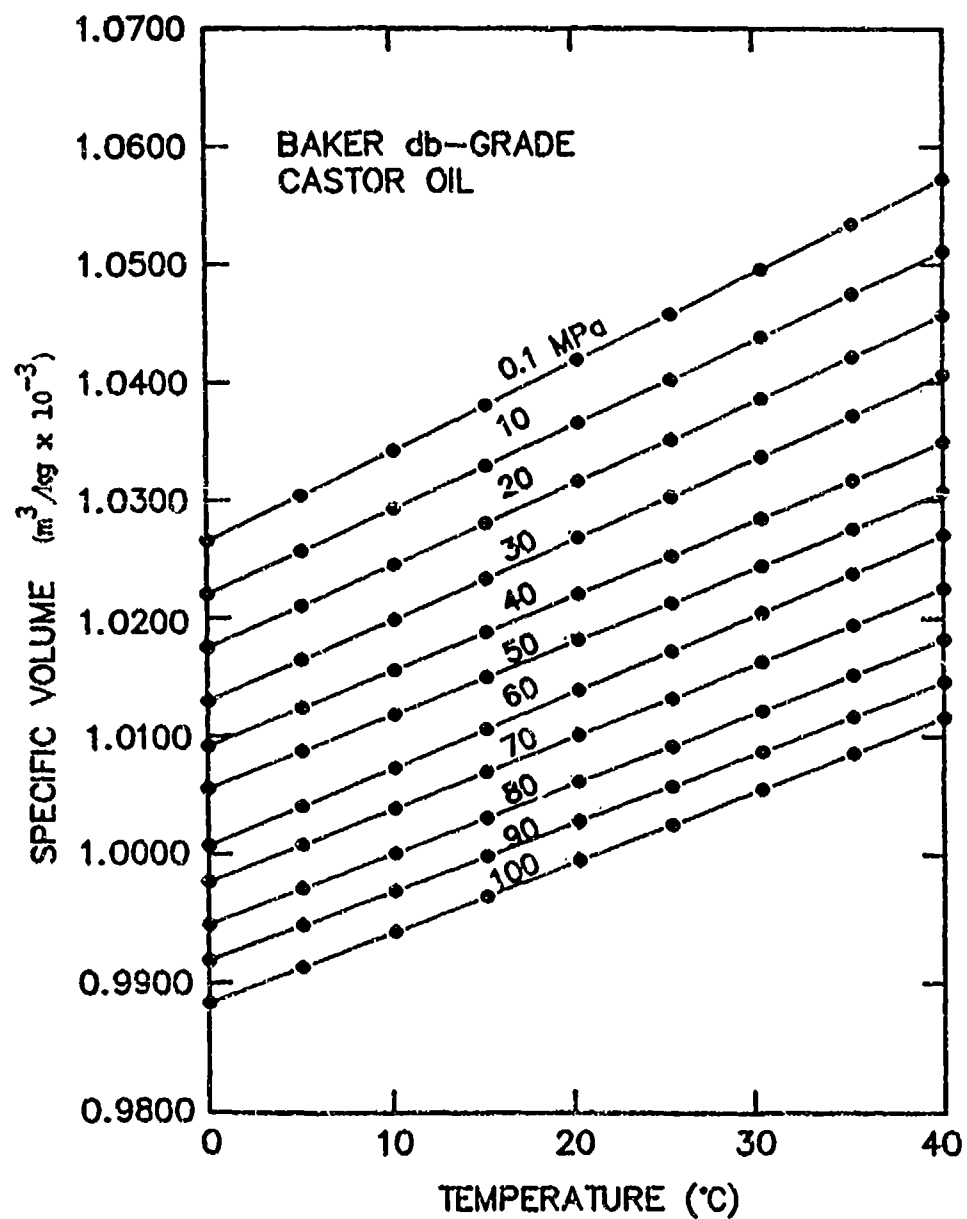


Fig. A5.8 - Specific volume vs temperature of Baker db-grade castor oil

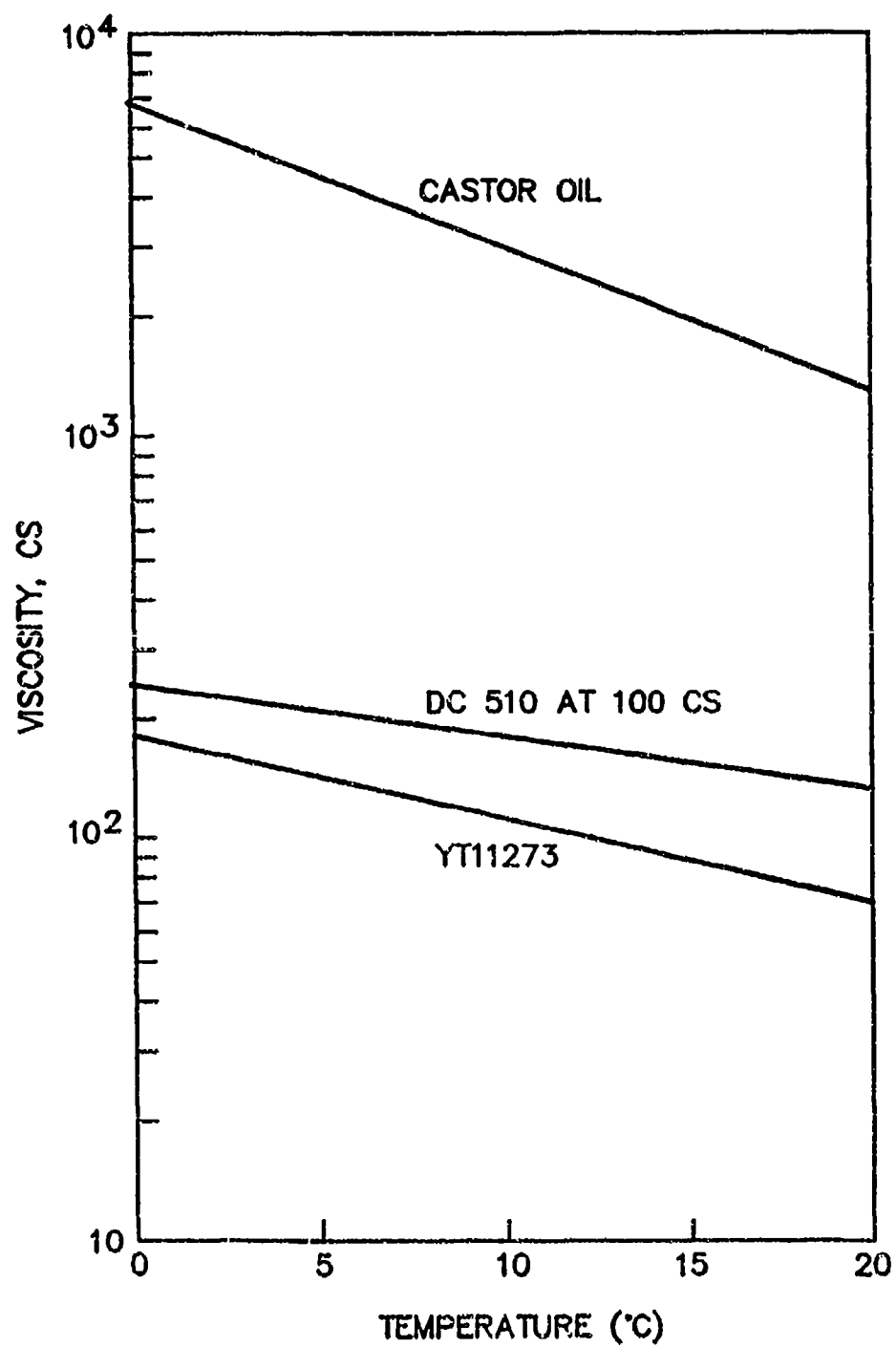


Fig. A5.4 - Viscosity as a function of temperature

DB grade castor oil is non-toxic. It is relatively messy to clean up, as it tends to leave a film of oil on surfaces that it has contacted. It is soluble in acetone, a 1:1 mixture by volume of acetone and methanol, and trichloroethane. It is not suitable for sewer disposal.

Lubricin N-1 castor oil is primarily a glyceryl tri-ricinoleate. Its principal advantage over DB grade is its much lower viscosity. It is approximately 30 centistokes³⁸⁹ at 25°C, increasing to only 96 centistokes at 0°C. Its density³⁸⁹ is 923 kg/m³ at 25°C. Thomas³⁹⁰ measured its sound speed as 1519 - 3.18T, where T is in °C. Green³⁸⁹ reported values of 1530 m/s at 0°C and 1458 m/s at 25°C. Timme³⁹¹ measured a volume resistivity of only 5.2x10⁹ ohm·cm for this material, while Green obtained a value higher than that of DB grade castor oil.

Lubricin has been reported as being less compatible with certain elastomers than DB grade³⁹². It is compatible with butyl and chlorobutyl formulations but exhibits poor compatibility with certain neoprene and natural formulations. Comments concerning toxicity, cleanup, and disposal are the same as those for DB grade.

A5.3 ISOPAR

Isopar is a trade name for hydrocarbon solvents manufactured by Exxon. Isopar L and Isopar M are the two liquids often used in towed arrays. These differ in their average molecular weight.

Isopar L is a narrow boiling fraction of highly branched, saturated hydrocarbons with an average molecular weight of 171 g/mol. It is a positively buoyant material with a density listed by the manufacturer as 777.5-0.74T, where the density is in kg/m³ and T is in °C. Its sound speed is also lower than that of water (1342-4.0T m/s)³⁹⁰.

Other physical properties that are listed by the manufacturer include a viscosity of 2.87 centipoise at 0°C, a surface tension of 0.0231 N/m at 25°C, a vapor pressure of 4.1x10³ Pa at 38°C, and a water solubility limit of 0.01%.

Isopar M is a similar type of material that is described by the manufacturer as a narrow-boiling fraction of highly branched, saturated hydrocarbons with an average molecular weight of 191 g/mole. Its physical properties are very similar to those of Isopar L. Its density is given by the manufacturer as $789.0 - 0.72 T$, where the density is in kg/m^3 and the temperature is in $^{\circ}\text{C}$. Its sound speed has been determined³⁹⁰ to be 1359-3.9T. The viscosity is listed by the manufacturer as 2.46 centipoise at 25°C , while its vapor pressure is the same as Isopar L. It also has the same water solubility limit. Its surface tension is given as 0.0248 N/m.

Since Isopar L and Isopar M are very similar chemically, their effects upon polymeric materials would be expected to be virtually identical. Neither would be considered to be suitable for use with butyl or chlorobutyl formulations, as they would most likely cause severe swelling. Likewise, it would be expected that most EPDM and natural rubber compounds would be unsuited for use with these materials. Nitrile formulations would probably exhibit fair to good compatibility.

Of the commercially available polyurethanes, PR 1538³⁸⁷ and PR 1592³⁵⁹ have fair to good compatibility with Isopar M. PR 1574, as well as Conathane EN 5 and EN 9 are unsuited for use in this material³⁵⁹. Other types of materials, such as cork-rubber composites (DC100, LC800, and NC775) also exhibit poor long-term compatibility with Isopar³⁸⁸.

Isopar L and Isopar M have possible toxicity if ingested and are skin irritants. Additionally, they are combustible materials and should be treated as a hazardous waste if and when discarded.

A5.3.1 Polyalkylene Glycol

Polyalkylene Glycol (PAG) is a monobutyl ether of polypropylene oxide with an average molecular weight of 600 g/mol. It normally contains small amounts of dodecyl succinic anhydride as an antioxidant. The material that is normally used as an acoustic transfer medium is marketed by Union Carbide under the designation of LB135Y23.

PAG overcomes the viscosity disadvantage of DB castor oil, having a viscosity³⁸⁸ of 190 centipoise at 0°C. Its viscosity as a function of temperature is shown in Fig. A5.1 and can be calculated from the expression $\eta = 190 \times 10^{-0.0513T}$. Additionally, it has a relatively high cavitation level. Moffett³⁸³ determined the threshold to be 240 dB/re 1μPa but rapidly dropping to 227 dB.

The density³⁹³ of PAG is relatively close to that of water and can be expressed as a function of temperature by the relation $\rho = 996.2 - 1.1T + 6.2 \times 10^{-3}T^2$, where ρ is in kg/m³ and T is in °C. Its sound speed³⁹³ in m/s has been measured as $1395 - 3.34T$, where T is the temperature in °C. PAG is a relatively incompressible material having an isothermal compressibility of 2.20×10^{-10} MPa⁻¹. Its surface tension³⁹³ is 0.063 N/m. It also has a low vapor pressure. Additionally, it is described by the manufacturer as having good stability toward oxidation and hydrolysis. It is also a relatively cheap material.

One of the principal disadvantages of PAG is that it has a relatively high water solubility. This will tend to alter its volume resistivity as a function of the amount of water that it absorbs. This can be expressed³⁹³ as $7.80 \times 10^{10} e^{6.1N}$, where N is the mole fraction of water.

PAG has good compatibility with butyl and chlorobutyl formulations, as well as nitriles. It has relatively poor compatibility with NR and EPDM formulations. It also has poor compatibility with PR 1538 and Cork-rubber composites³⁸⁸ (DC100, NC710, NC775, and LC800).

PAG is non-toxic, with no reported effects of eye or skin irritation. It is readily removed from surfaces with acetone, acetone-alcohol mixtures, or methyl ethyl ketone. Recommended mode of disposal is by incineration (to be performed only by a licensed disposal firm).

A5.3.2 Polyalphaolefin

Polyalphaolefin (PAO) is marketed by Uniroyal under the designation of PAO-20E. It is a polymer of 1-octene, with an average molecular weight of 1015 g/mol. As such, it can be considered an aliphatic hydrocarbon solvent.

Polyalphaolefin has a lower density than that of water. Its density as a function of temperature can be expressed³⁹⁴ as $856.0 - 0.63T$. Its measured sound speed³⁹⁰ is a relatively good match to that of water ($1532 - 3.6T$). It has a relatively low coefficient of volume thermal expansion, $7.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$. Its water solubility limit³⁸⁷ is 0.002%.

Polyalphaolefin has a moderately high viscosity, 548 centipoise at 21°C . It has a very high volume resistivity, greater than 10^{15} ohm-cm. Additionally, it has a low vapor pressure.

Since PAO is an aliphatic hydrocarbon solvent, it can be expected to have poor compatibility with most butyl and chlorobutyl formulations, as well as CR's and NR's. One would also expect the material to be fairly incompatible with EPDM, and to have fair compatibility with NBR formulations. Polyalphaolefin has marginal compatibility³⁸⁷ with PR 1538.

Polyalphaolefin has excellent stability to hydrolysis and oxidation. It is inexpensive and non-toxic. It is also moderately easy to remove from surfaces, being soluble in petroleum ether and trichloroethane. The recommended mode of disposal is by incineration.

A5.3.3 Shell Sol 71

Shell Sol 71 is a petroleum distillate containing 95.9% saturated hydrocarbons and 4.1% olefins that is marketed by Shell Chemical Company. Due to its positive buoyancy, it is sometimes used as a fill fluid in towed arrays.

Shell Sol is a relatively volatile material, having a vapor pressure of approximately 700 Pa at normal room temperature. Its density is less than that of water (756 kg/m^3 at 16°C). Its sound speed is also considerably lower³⁹¹ than that of water (1216 m/s at 28°C). Shell Sol has a surface tension³⁸⁷ of 0.0844 N/m .

Since Shell Sol is primarily a hydrocarbon solvent, many of the statements made earlier with regard to Isopar are also applicable to it. It can be expected to be largely incompatible with butyl and chlorobutyl formulations, causing severe swelling. It probably will adversely affect most amine and NR compounds. Nitrile and fluorocarbon rubbers would be expected to fare somewhat better. Shell Sol has fair compatibility³⁵⁹ with PR 1502. It is unsuited for use with PR 1574, EN 5, EN 9, and Goodrich castable Rho-0.

Shell Sol is a minor eye and skin irritant and probably has toxic effects if ingested. It is combustible, and should be treated as a hazardous waste when discarding.

AB.3.4 Silicone Fluids

The specific materials upon which data are included here are a series of silicone fluids manufactured by Dow Corning. These are the DO 200 series and DO 510/100 silicones. The manufacturer recommends that the materials be disposed of by mixing with a large quantity of combustible materials and burning.

The DO 200 series is a group of polydimethylsiloxanes that differ in their molecular weights and viscosities. DO 200.5 is a polydimethylsiloxane with a viscosity of 4.8 centipoise at 4.8°C . It has a density of 920 kg/m^3 at 28°C . Its sound speed as a function of temperature has been determined³⁸⁷ to be $(1040 + 3.08T) \text{ m/s}$, where T is the temperature in $^\circ\text{C}$. It is only slightly volatile, with a vapor pressure of 0.004 Pa at 70°C . Its coefficient of volume thermal expansion is $0.00106^\circ\text{C}^{-1}$. The surface tension is reported to be 0.0017 N/m at 28°C . The acoustic attenuation of this material becomes significant only at high frequencies³⁸⁹.

There is relatively little data on compatibility of these materials with specific rubber formulations. However, based upon the general guidelines of Larsen^{311,395}, one would expect these fluids to have good to fair compatibility with the majority of elastomer classes, with the exception of polysulfides and silicone elastomers. Generalizations about urethane elastomers are very difficult to make, due to the wide variety of materials from which they can be compounded.

Silicone fluid DC200.5 is non-toxic and non-irritating. It has good oxidative stability and is soluble in methyl ethyl ketone, ethyl ether, carbon tetrachloride, toluene, trichloroethane, turpentine, and xylene.

The type DC 200.20 has a viscosity of 19 centipoise at 25°C. Its density is 949 kg/m³ at 25°C. Its sound speed is much lower³⁹⁰ than that of water (1065 - 293T, where T is the temperature in degrees Centigrade). Its acoustic attenuation becomes significant only at high frequencies. Its coefficient of volume thermal expansion is 0.00107°C⁻¹. Its surface tension is 0.0206 N/m at 25°C. It is also reported to have very low vapor pressure. The same general comments can be made for it as for DC 200.5 regarding its compatibility and solubility properties. It is reported to be a non-toxic eye irritant.

Type DC 200.100 is a polydimethylsiloxane with a viscosity of 98 centipoise at 25°C. Its density as a function of temperature³⁸⁷ has been determined to be (984.4 - 0.88T) kg/m³, where T is the temperature in °C. It also has a much lower sound speed³⁹⁰ than that of water, 1078 - 2.87T. Its surface tension is 0.0209 N/m at 25°C. The coefficient of volume expansion is 0.00098°C⁻¹. Its compatibility, solubility, and toxicity properties are similar to that of DC 200.20.

Type DC 200.1000 is a polydimethylsiloxane with a viscosity of 971 centipoise at 25°C. Its density is 972 kg/m³ at 25°C. Its sound speed³⁹⁰ is (1074 - 2.78T) m/s, where T is the temperature in °C. Its acoustic attenuation becomes significant only at high frequencies. The coefficient of volume thermal expansion is 0.00098°C⁻¹. Its surface tension is 0.0212 N/m at 25°C. It is also a non-toxic eye irritant.

Type DC 510.100 is a polymethylphenylsiloxane with a viscosity of 99.2 centipoise³⁶⁸ at 25°C. Its density as a function of temperature has been reported³⁶⁸ to be $(1006.6 - 0.87T)$ kg/m³, where T is the temperature in °C. The material has a relatively high volume resistivity of 2×10^{15} ohm·cm. Green has measured the sound speed, acoustic impedance, and viscosity of this material as a function of temperature. These are shown in Figs. A5.1, A5.2, and A5.4. This material is reported³⁶⁸ to cavitate at 1/3 the intensity of water and to have measurable acoustic attenuation above 50 kHz. Green has reported that DC 510.100 is incompatible with some types of elastomers, although specifics are not given. It is also a skin and eye irritant. As with the other silicone fluids, it is somewhat difficult to remove from transducer parts. The recommended mode of disposal is by incineration (only by a licensed firm!).

**APPENDIX 6 - SOUND SPEEDS, DENSITIES, AND
CHARACTERISTIC IMPEDANCES OF VARIOUS METALS[†]**

METALS	SOUND SPEEDS			DENSITY ρ (kg/m ³)	CHARACTERISTIC
	LONGITUDINAL				BULK
	BULK	BAR	SHEAR		IMPEDANCE
	m/s	m/s	m/s		$\rho \cdot c$ (kg/m ² s)
	($\times 10^3$)	($\times 10^3$)	($\times 10^3$)	($\times 10^3$)	($\times 10^6$)
Aluminum	6.40	5.15	3.13	2.7	17.3
Beryllium	12.89	8.88	1.8	23.2
Brass, 70-30	4.37	3.40	2.10	8.5	37.0
Cast Iron	3.50-5.60	3.0-4.7	2.2-3.2	7.2	25.0-40.0
Copper	4.80	3.65	2.33	8.9	42.5
Gold	3.24	2.03	1.20	19.3	63.0
Iron	5.96	5.18	3.22	7.9	46.8
Lead	2.40	1.25	0.79	11.3	27.2
Magnesium	5.74	4.90	3.08	1.7	9.9
Mercury	1.45	13.6	19.6
Molybdenum	6.25	3.35	10.2	63.7
Nickel	5.48	4.70	2.99	8.9	48.5
Platinum	3.96	2.80	1.67	21.4	85.0
Steel, Mild	6.10	5.05	3.24	7.9	46.7
Silver	3.70	2.67	1.70	10.5	36.9
Tin	3.38	2.74	1.61	7.3	24.7
Titanium	5.99	3.12	4.50	27.0
Tungsten	5.17	2.88	19.3	100.0
Uranium	3.37	2.02	18.7	63.0
Zinc	4.17	3.81	2.48	7.1	29.6
Zirconium	4.65	2.30	6.4	29.8

Other Solid Materials:

Crown Glass	5.86	5.30	3.42	2.5	14.0
Granite	3.95	2.75
Ice	3.98	1.99	0.9	3.6
Nylon	1.8-2.2	1.1-1.2	2.0-2.7
Parafin, Hard	2.2	0.83	1.8
Plexiglas/Lucite	2.36	1.8	1.32	1.20	3.2
Polystyrene	2.07	1.06	2.8
Quartz, Fused	5.57	5.37	3.52	2.6	14.5
Teflon	1.35	2.2	3.0
Tungsten Carbide	6.06	3.98	10.0-15.0	60.6-98.6
Wood, Oak	4.1	0.8

(continued)

Appendix 6 (continues)

METALS	SOUND SPEEDS			DENSITY ρ (kg/m ³)	CHARACTERISTIC
	LONGITUDINAL				BULK
	BULK	BAR	SHEAR		IMPEDANCE
	$\rho \cdot c$	$\rho \cdot c$	$\rho \cdot c$		$\rho \cdot c$
	m/s	m/s	m/s		(kg/m ² s)
	($\times 10^3$)	($\times 10^3$)	($\times 10^3$)	($\times 10^3$)	($\times 10^6$)
<u>Fluids:</u>					
Benzene	1.32	0.88	1.16
Castor Oil	1.54	0.95	1.45
Glycerin	1.92	1.26	2.5
Methyl Iodide	0.98	3.23	3.2
Oil, SAE 20	1.74	0.87	1.5
Water, Fresh	1.48	1.00	1.48

† (From J.R. Fredrick, "Ultrasonic Engineering", p. 363, John Wiley & Sons, Inc., New York; 1985.)

APPENDIX 7 - APPROXIMATE RELATIONSHIP BETWEEN SHORE A HARDNESS AND STATIC YOUNG'S MODULUS

It is well known that the elastic modulus and hardness of an isotropic, crosslinked rubber are related. The relationship between the International Rubber Hardness degrees (ASTM D 1415-68) and Young's modulus has been shown by Gent³⁹⁶ to be an exact one. Only an approximate relationship has been found for the Shore A hardness scale. However, as the readings in I.R.H. are very nearly identical to those in the Shore A durometer test, the relationship in the following graph (Fig. A7.1) will be a useful indicator of the static Young's modulus from Shore A hardness measurements.

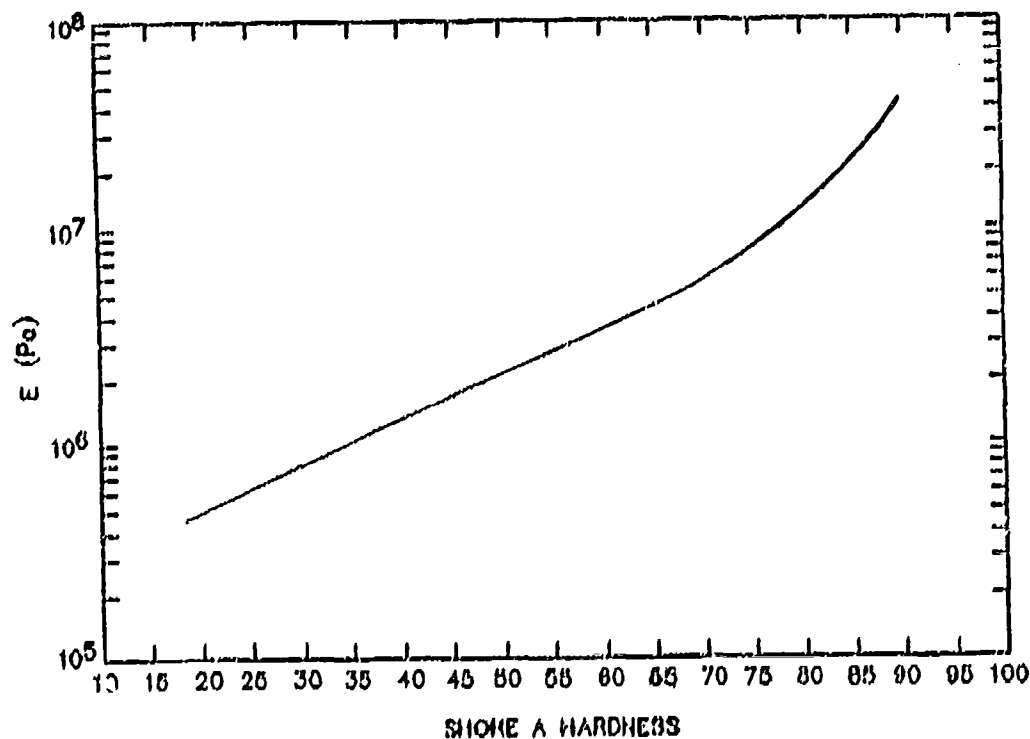


Fig. A7.1 - Approximate relationship between Shore A hardness and static Young's modulus

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**APPENDIX 8 - SOME MECHANICAL AND PHYSICAL PROPERTIES
OF VARIOUS ALLOYS†**

Alloy	Ultimate tensile strength	0.2 % Yield	Elonga- tion in 5 cm (2 in.)	Modulus of elas- ticity	Density	Strength/wt (yield/dens)
	$\frac{\text{MN}}{\text{m}^2}$ ksi	$\frac{\text{MN}}{\text{m}^2}$ ksi	(%)	$\frac{10^3 \text{ MN}}{\text{m}^2}$ 10 ³ ksi	$\frac{10^3 \text{ kg}}{\text{m}^3}$ lb/in. ³	$\frac{10^2 \text{ m}}{10^3 \text{ in.}}$
Berylco 717c (aged)	758.4 110	517.1 75	7	152 22	8.91 0.322	59.2 233
Std 70-30 Cu-Ni MIL-C-20159-1	413.7 60	220.6 32	20	152 22	8.91 0.322	25.3 99
5% Ni-Al Bronze MIL-B-16033-1(4) (heat treated)	758.4 110	413.7 60	5	131 19	7.72 0.279	54.7 215
316 Stainless MIL-S-18262-3	482.6 70	206.8 30	30	200 28	8.02 0.290	26.3 103
Ni-Al Bronze MIL-B-21230-1	586.1 85	241.3 35	15	131 19	7.53 0.272	32.7 129
Mn-Ni-Al Bronze MIL-B-21230-2	620.6 90	275.8 40	20	124 18	7.53 0.272	37.4 147
Armco 22-13-5 Stainless*	827.4 120	448.2 65	45	200 29	7.89 0.285	57.9 228
7075-T6 Aluminum	572.3 82	503.3 73	11	71.7 10.4	2.80 0.101	183.4 722
6061-T6 Aluminum	310.3 45	275.8 40	12	68.9 10.0	2.71 0.098	103.8 408
5086-H34 Aluminum	324.1 47	255.1 37	10	71.0 10.3	2.66 0.096	97.8 385
5083-O Aluminum	289.6 42	144.8 21	22	71.0 10.3	2.66 0.098	55.6 218

*Annealed at 2050°F (1121°C) and water quenched

†Taken from I. D. Groves, Jr., "The Design of Deep-Submergence Hydrophones," NRL Report No. 7339, 3 Sept 1971.

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**APPENDIX 9 - TYPICAL CORROSION RATES AND PITTING
CHARACTERISTICS OF VARIOUS METALS AND ALLOYS IN SEAWATER†**

Material	Corrosion rate (mean range)	Resistance to pitting	Typical rate of penetration in pits
70-30 Cu-Ni ^a	0.2-3.8×10 ⁻² mm/yr 0.1-1.5 mils/yr	Good	2.5-13×10 ⁻² mm/yr 1-5 mils/yr
Copper ^a	1.2-7.6×10 ⁻² mm/yr 0.5-3.0 mils/yr	Good	15-30×10 ⁻² mm/yr 6-12 mils/yr
Ni-Al Bronze ^a	2.5-30×10 ⁻² mm/yr 1.0-12 mils/yr	Good	5-23×10 ⁻² mm/yr 2-9 mils/yr
Monel 400 ^a	b	Fair	13-30×10 ⁻² mm/yr 5-15 mils/yr
316 Stainless ^a	b	Fair	178×10 ⁻² mm/yr 70 mils/yr
Armco 22-13-5 Stainless ^c	Not available	Good	Unaffected after 9 mo in quiet seawater
Berylco 717C ^d	Reported by manufacturer to have virtually the same corrosion characteristics as Std 70-30 Cu-Ni alloy		
7075-T6 Aluminum ^e	b	Fair	28-51×10 ⁻² mm/yr 11-20 mils/yr Always needs protection
6061-T6 Aluminum ^e	b	Moderate	13-25×10 ⁻² mm/yr 5-10 mils/yr May need protection
5086-H34 Aluminum ^e	b	Excellent	<2.5×10 ⁻² mm/yr <1 mils/yr Usually unprotected
5083-O Aluminum ^e	b	Excellent	<2.5×10 ⁻² mm/yr <1 mils/yr Usually unprotected

^aH. H. Uhlig, *Corrosion Handbook* (John Wiley & Sons, New York, 1948).

^bCharacteristic form of corrosion makes overall weight-loss data meaningless, since failure occurs by pitting.

^cArmco Product Data S-45 (June 1970).

^dThe Beryllium Corp., Bulletin No. 4100 (1966).

^eR. E. Groover, T. J. Lennox, Jr., and M. E. Peterson, "Characterization of the Corrosion Behavior and Response to Cathodic Protection of Nineteen Aluminum Alloys in Sea Water," NRL Memorandum Report 1961, Jan 1969.

†Taken from I. D. Groves, Jr., "The Design of Deep-Submergence Hydrophones," NRL Report No. 7339, 3 Sept 1971.

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GLOSSARY

Abrasion Resistance (ASTM's D1630-61 and D2228-69) - This refers to the wear resistance of an elastomer and is usually measured by the amount of material lost when placed in contact with a moving abrasive surface. It is given as a volume-loss percentage when compared to a standard elastomer. A quantitative result is very difficult to obtain; and most elastomers are classified as poor, fair, good, or excellent.

Acoustic Impedance - The propagation of acoustic waves into and through a material depends on the density of the material and the speed of the acoustic waves within the material. The product of density and acoustic speed for a certain material is termed the specific acoustic impedance. Acoustic impedance is also the characteristic property that governs sound transmission from one medium to another, as from a liquid into a solid. The greater the impedance mismatch between two media, the lower will be the transmission of an acoustic wave from one to the other. Practically speaking, the impedance mismatch between transducer elastomers and fluids is not usually a critical factor in the audio-frequency and low ultrasonic range. This will depend upon the geometry and stiffness of the material. For transducers operating at higher frequencies, the acoustic impedance of a window material is an important consideration.

The speed of an acoustic wave in a material is directly proportional to the square root of the governing modulus. The governing modulus is the modulus associated with the particular mode of wave propagation; i.e., shear modulus (G) governs the propagation of shear waves while bulk modulus (K) and the longitudinal modulus (M) govern the propagation of bulk and plane waves, respectively. The relationship between modulus and acoustic velocity is given by $R = \rho(\underline{c})^2$ where R represents a generic modulus, ρ is material density, and \underline{c} is acoustic velocity.

Compression Set (ASTM's D395-78 and D1229-79) - This is the residual deformation that remains in a body after removal of a compressive stress.

Dielectric Strength (ASTM D149-81) - This is the ability of a dielectric material to separate charges of a potential difference. It is the ratio of breakdown voltage to sample thickness.

Electric Dissipation Factor (ASTM D150-81) - This is the ratio of the parallel reactance to the parallel resistance. It is related to the energy dissipated and, therefore, to the efficiency for insulating materials.

Hardness (ASTM D2240-81) - This is an indication of the resistance of an elastomer to deformation. It is determined by pressing a ball or rounded tool into the surface of the elastomer. The resistance is measured on various scales covering very soft elastomers to very hard ones. These measurements are designated by a Shore Hardness scale A or D and given values of 0 to 100 within each scale. Shore A is used for soft elastomers and Shore D for hard elastomers.

Hysteresis - This refers to the energy lost per loading cycle in the cyclic deformation of rubber. The mechanical loss of energy is converted into heating of the rubber.

Low-Temperature Stiffness (ASTM's D832-79 and D1053-79) - The low-temperature stiffening point is the temperature at which Young's modulus reaches 10,000 psi or 68.9 MPa. In general, the softer the material, the lower the stiffening temperature will be.

Ozone Resistance (ASTM's D3395-82 and D1149-81) - This is the resistance of elastomeric materials to cracking and oxidation under high atmospheric ozone concentrations. This property is indicative of the ability of a material to exist in a high corona environment without exhibiting extensive oxidative degradation.

Relative Dielectric Constant (ASTM D150-81) - This is the ratio of the dielectric constant of the material ϵ_m to that of free space ϵ_0 . It is usually measured by determining the parallel-plate-capacitance with the material between the plates C_m and the capacitance with a vacuum between the plates C_0 .

Scorch - This is the premature vulcanization of a rubber compound. It may be brought about by heat generated during the mixing of a rubber compound or by extremely reactive cure systems in compounded elastomers that are stored at room temperature.

Tear Strength (Resistance) (ASTM D624) - This is a measure of the stress needed to continue tearing a sheet of rubber, usually after an initiating cut.

Tensile Strength (ASTM's D412-80 and D638) - In elastomers this refers to the force per unit of original cross-sectional area required to elongate to rupture.

300% Modulus (ASTM D412-80) - (Tensile stress at given elongation.) In elastomers this refers to the force per unit of original cross-sectional area to produce a total extension of 300%. Other elongations have also been used. It is a ratio of the stress applied to the strain induced but is not a measure of Young's modulus. Also, it is not related to hardness.

Ultimate Elongation (ASTM D412-80) - This is the maximum extension in percent of an elastomer at the instant of rupture.

Vapor Pressure (ASTM's D323-72 and D2551-71) - This is the absolute pressure exerted by a vapor in equilibrium above a solid or liquid.

Viscosity (ASTM D1646-81) - This is the resistance of fluids to a change of form. It is expressed in Pascal-seconds. For a polymeric fluid, the viscosity values depend upon the size and configurations of the polymer molecules. A change in observed viscosity is used as an indicator of the onset of vulcanization. Measured viscosity values may also be correlated with the molecular weight or molecular size.

Volume Resistivity (ASTM D991-82) - This is the resistance to current leakage through the sample.

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FIGURES

Chapter 1:

Fig. 1.1a.....	Simple shear deformation of an isotropic, viscoelastic element.....	5
Fig. 1.1b.....	Time profile of sinusoidal stress and strain.....	5
Fig. 1.1c.....	Vectorial resolution of complex shear modulus in sinusoidal deformation.....	5
Fig. 1.2a.....	Bulk compression.....	7
Fig. 1.2b.....	Bulk longitudinal deformation.....	7
Fig. 1.2c.....	Simple extension.....	7
Fig. 1.3.....	Variation of storage modulus and loss tangent with temperature and frequency for a viscoelastic material.....	13
Fig. 1.4.....	Plot of storage Young's modulus vs reduced frequency at three different temperatures for a resin-cured chlorobutyl reinforced with 35 phr of N347 black.....	14
Fig. 1.5.....	Plot of loss tangent vs reduced frequency at three different temperatures for a resin-cured chlorobutyl reinforced with 35 phr of N347 black.....	14

Chapter 2:

Fig. 2.1.....	Block diagram of impedance tube measurement system....	35
Fig. 2.2.....	Block diagram of transmit-time measurement system....	38
Fig. 2.3.....	Block diagram of Michelson interferometer.....	42
Fig. 2.4a.....	External reflection.....	47
Fig. 2.4b.....	Multiple external reflection.....	47
Fig. 2.4c.....	Attenuated total reflection.....	48
Fig. 2.4d.....	Photoacoustic effect.....	50
Fig. 2.5.....	Thermogravimetric analysis curve for chlorobutyl elastomer.....	58

Chapter 3:

Fig. 3.1.....	Effect of crosslink density on vulcanizate properties (after Refs. 229 and 232). (This is a modified version of Fig. 6 in Ref. 70.).....	62
Fig. 3.2.....	Plot of Shore A hardness vs carbon black loading for Neoprene GRT compound reinforced with N550 black.....	65
Fig. 3.3.....	Effect of dynamic shear strain on the dynamic modulus and loss factor of a typical elastomer (after Ref. 70).....	65
Fig. 3.4.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Neoprene WRT at various loadings of N660 black (phr = parts per hundred of rubber)	66
Fig. 3.5.....	Plot of storage Young's modulus vs carbon black particle size at 30 parts loading for Neoprene GRT formulations at 1000 Hz and 283.15K.....	68
Fig. 3.6.....	Plot of longitudinal modulus vs carbon black particle size at 30 parts loading for Neoprene GRT formulations at 1.8 MHz and 298.15K.....	68
Fig. 3.7.....	a. Compression molding..... b. Injection molding..... c. Transfer molding.....	78 79 79

Chapter 4:

Fig. 4.1.....	Simple mount system.....	91
Fig. 4.2.....	Plot of calculated transmissibility vs frequency at 263.15K for red lead-cured chlorobutyl reinforced with no black and 35 phr of three types of black.....	93
Fig. 4.3.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for red lead-cured chlorobutyl reinforced with no black and 35 phr of three types of black.....	93
Fig. 4.4.....	Plot of loss tangent vs reduced frequency at 283.15K for red lead-cured chlorobutyl reinforced with no black and 35 phr of three types of black.....	94
Fig. 4.5.....	Plot of calculated transmissibility vs frequency at 263.15K for resin-cured chlorobutyl reinforced with no black and three loadings of N347 black.....	94

Fig. 4.6.....	Use of a viscoelastic layer in damping: (a) extensional type and (b) simple three- layer constrained shear type.....	96
Fig. 4.7.....	Calculated structural loss factor vs frequency at 263.15K for extensional damping of 0.95-cm brass coated with 1.2-cm red lead-cured chlorobutyl reinforced with no black and three different types of black.....	98
Fig. 4.8.....	Calculated structural loss factor vs frequency at 263.15K for same formulations as in Fig. 4.7 on a 0.95-cm steel backing.....	98
Fig. 4.9.....	Calculated structural loss factor vs frequency at 263.15K for extensional damping of 0.95-cm brass coated with 1.2-cm resin-cured chlorobutyl at various loadings of N347 black.....	100
Fig. 4.10.....	Effect of temperature on extensional damping on 1.2-cm resin-cured chlorobutyl reinforced with 35 phr N347 black on 0.95-cm brass backing.....	100
Fig. 4.11.....	Calculated structural loss factor vs frequency for constrained-layer configuration at 263.15K using 2.5-cm base plate, 0.20-cm cover, and 0.10-cm resin-cured chlorobutyl at various loadings of N347 black.....	101
Fig. 4.12.....	Calculated structural loss factor vs frequency for same formulations and conditions as in Fig. 4.11 at 283.15K.....	101
Fig. 4.13.....	Calculated structural loss factor vs frequency as a function of temperature for resin-cured chlorobutyl reinforced with 35 phr N347 with same constrained-layer configuration as Figs. 4.11 and 4.12.....	102
 <u>Chapter 5:</u>		
Fig. 5.1.....	Plot of storage Young's modulus vs reduced frequency for Butyl 70821 at three temperatures.....	108
Fig. 5.2.....	Plot of loss tangent vs reduced frequency for Butyl 70821 at three temperatures.....	109
Fig. 5.3.....	Longitudinal wave speed at 7 kHz as a function of temperature and pressure for Chlorobutyl 7082A.....	113

Fig. 5.4.....	Plot of storage Young's modulus vs reduced frequency for Chlorobutyl H862A at three different temperatures.....	113
Fig. 5.5.....	Plot of loss tangent vs reduced frequency for Chlorobutyl H862A at three different temperatures.....	114
Fig. 5.6.....	Plot of storage Young's modulus vs reduced frequency for red lead-cured (—) and resin-cured (----) chlorobutyls at 283.15K reinforced with 50 phr N660 black.....	115
Fig. 5.7.....	Plot of loss tangent vs reduced frequency for red lead-cured (—) and resin-cured (----) chlorobutyls at 283.15K reinforced with 50 phr N660 black.....	116
Fig. 5.8.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for resin-cured chlorobutyl reinforced with no black and three different loadings of N347 black.....	118
Fig. 5.9.....	Plot of loss tangent vs reduced frequency at 283.15K for resin-cured chlorobutyl reinforced with no black and three different loadings of N347 black.....	119
Fig. 5.10.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for resin-cured chlorobutyl reinforced with 35 phr N347 black and 0 phr of Mica (1) and different loadings of Mico-Mica C1000 (2 = 30 phr, 3 = 15 phr, 4 = 45 phr).....	122
Fig. 5.11.....	Plot of loss tangent vs reduced frequency at 283.15K for resin-cured chlorobutyl with 35 phr N347 black and 0 phr of Mica (1) and different loadings of Mico-Mica C1000 (2 = 30 phr, 3 = 15 phr, 4 = 45 phr).....	122

Chapter 6:

Fig. 6.1.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for peroxide-cured EPDM's at three different loadings of N660 black.....	131
Fig. 6.2.....	Plot of loss tangent vs reduced frequency at 283.15K for peroxide-cured EPDM's at three different loadings of N660 black.....	131
Fig. 6.3.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for optimized peroxide-cured EPDM.....	134

Fig. 6.4.....	Plot of loss tangent vs reduced frequency at three temperatures for optimized peroxide-cured EPDM.....	134
Fig. 6.5.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Royalene 400 EPDM.....	135
Fig. 6.6.....	Plot of loss tangent vs reduced frequency at three temperatures for Royalene 400 EPDM.....	135

Chapter 7:

Fig. 7.1.....	Plot of shear storage modulus (—) and loss tangent (---) vs reduced frequency at 295.85K for Viton A.....	139
Fig. 7.2.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Viton B-50.....	139
Fig. 7.3.....	Plot of loss tangent vs reduced frequency at three temperatures for Viton B-50.....	140
Fig. 7.4.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Viton B-910.....	141
Fig. 7.5.....	Plot of loss tangent vs reduced frequency at three temperatures for Viton B-910.....	141

Chapter 8:

Fig. 8.1.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-4.....	149
Fig. 8.2.....	Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 165-4.....	150
Fig. 8.3.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-5.....	150
Fig. 8.4.....	Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 165-5.....	151
Fig. 8.5.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation AA 165-6.....	151

Fig. 8.6.....	Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation AA 100-0.....	162
Fig. 8.7.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for natural rubber formulation 334-201.....	162
Fig. 8.8.....	Plot of loss tangent vs reduced frequency at three temperatures for natural rubber formulation 334-201.....	163

Chapter 9:

Fig. 9.1.....	Plot of longitudinal storage modulus vs carbon black particle size for Neoprene GRT formulations with 30 phr loading at 298.05K and 3.15 MPa over the 4-kHz through 10-kHz range.....	100
Fig. 9.2.....	Plot of loss tangent vs reduced frequency for Neoprene WRT at 283.15K with various loadings of N660 black.....	100
Fig. 9.3.....	Effect of increased carbon black loading on longitudinal storage modulus for Neoprene WRT reinforced with N660 black.....	101
Fig. 9.4.....	Comparison of storage Young's modulus vs reduced frequency at 283.15K for Neoprene GRT and WRT formulations reinforced with 30 phr PEP 530 black.....	101
Fig. 9.5.....	Comparison of loss tangent vs reduced frequency at 283.15K for Neoprene GRT and WRT formulations reinforced with 30 phr PEP 530 black.....	102
Fig. 9.6.....	Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) at 283.15K for Durka 5112 black.....	102
Fig. 9.7.....	Plot of storage Young's modulus vs reduced frequency at three reference temperatures for DTNARD0 Neoprene 334-292.....	105
Fig. 9.8.....	Plot of loss tangent vs reduced frequency at three reference temperatures for DTNARD0 Neoprene 334-292.....	105

Chapter 10:

Fig. 10.1.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Parkerll OLT formulations with different loadings of N660 black.....	171
----------------	--	-----

Fig. 10.2.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with different loadings of N550 black.....	171
Fig. 10.3.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of iron oxide filler.....	173
Fig. 10.4.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of iron oxide filler.....	173
Fig. 10.5.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of silica filler	176
Fig. 10.6.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with two different loadings of silica filler.....	176
Fig. 10.7.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of peroxide curing coagent.....	178
Fig. 10.8.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of peroxide curing agent.....	178
Fig. 10.9.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of different peroxide curing coagent.....	180
Fig. 10.10.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying amounts of different peroxide curing coagent.....	180
Fig. 10.11.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for Paracril CLT formulations with peroxide cure and three different fillers.....	182
Fig. 10.12.....	Plot of loss tangent vs reduced frequency at 283.15K for Paracril CLT formulations with varying peroxide cures and three different fillers.....	182
Fig. 10.13.....	Plot of storage Young's modulus vs reduced frequency at 283.15K for nitrile formulations with varying AON content.....	185
Fig. 10.14.....	Plot of loss tangent vs reduced frequency at 283.15K for nitrile formulations with varying AON content.....	185

Fig. 10.15.....Plot of storage Young's modulus vs reduced frequency at 283.15K for 26% ACN formulations with varying amounts of N550 black.....187

Fig. 10.16.....Plot of loss tangent vs reduced frequency at 283.15K for 26% ACN formulations with varying amounts of N550 black.....187

Chapter 11:

Fig. 11.1.....Schematic of formation of polyurethane.....190

Fig. 11.2.....Plot of storage Young's modulus vs reduced frequency at three different reference temperatures for PR 1526.....192

Fig. 11.3.....Plot of loss tangent vs reduced frequency at three different reference temperatures for PR 1526.....193

Fig. 11.4.....Plot of storage Young's modulus vs reduced frequency at three different reference temperatures for PR 1528.....193

Fig. 11.5.....Plot of loss tangent vs reduced frequency at three different reference temperatures for PR 1528....194

Fig. 11.6.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1538...194

Fig. 11.7.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1547...195

Fig. 11.8.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1564...195

Fig. 11.9.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1570...196

Fig. 11.10.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1574...196

Fig. 11.11.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1590...197

Fig. 11.12.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for PR 1592...197

Fig. 11.13.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for EN 5.....198

Fig. 11.14.....Plot of storage Young's modulus (E') and loss tangent ($\tan \delta$) vs reduced frequency at 283.15K for EN 9.....198

Fig. 11.15.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Uralite 3140.....	199
Fig. 11.16.....	Plot of loss tangent vs reduced frequency at three temperatures for Uralite 3140.....	199
Fig. 11.17.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Sorbothane (50 shore 00 durometer).....	200
Fig. 11.18.....	Plot of loss tangent vs reduced frequency at three temperatures for Sorbothane (50 shore 00 durometer).....	200
Fig. 11.19.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Sorbothane (70 shore 00 durometer).....	201
Fig. 11.20.....	Plot of loss tangent vs reduced frequency at three temperatures for Sorbothane (70 shore 00 durometer).....	201

Chapter 12:

Fig. 12.1.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for polybutadiene.....	216
Fig. 12.2.....	Plot of loss tangent vs reduced frequency at three temperatures for polybutadiene.....	216
Fig. 12.3.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for Hypalon 40.....	217
Fig. 12.4.....	Plot of loss tangent vs reduced frequency at three temperatures for Hypalon 40.....	217
Fig. 12.5.....	Plot of storage Young's modulus vs reduced frequency at three temperatures for styrene butadiene formulation AA 185-8.....	218
Fig. 12.6.....	Plot of loss tangent vs reduced frequency at three temperatures for styrene butadiene formulation AA 185-8.....	218

Appendix 5:

Fig. A5.1.....	Velocity of sound as a function of temperature.....	247
Fig. A5.2.....	Acoustic impedance as a function of temperature.....	248

Elastomeric Materials for Acoustical Applications

Fig. A5.3.....Specific volume vs temperature of Baker dB-grade
castor oil.....252

Fig. A5.4.....Viscosity as a function of temperature.....253

Appendix 7:

Fig. A7.1.....Approximate relationship between Shore A hardness and
static Young's modulus.....263

TABLES

Chapter 3:

3.1.....Factors Involved in the Selection of Polymers.....	58
3.2.....Aging Properties of Different Types of Elastomers.....	74

Chapter 5:

5.1.....Butyl 70821.....	110
5.2.....Formulations for Chlorobutyl Cure Systems.....	111
5.3.....Formulation and Physical Properties for Chlorobutyl H862A.....	112
5.4.....Physical Properties Obtained from Four Different Crosslinking Systems with No Black and 50-phr Loadings of GPF (N660) Black and MT (N990) Blacks.....	117
5.5.....Physical Properties Obtained from Various Carbon Blacks at 35-phr Loading in Red Lead-Ethylene Thiourea Cure Modified with 0.5-phr Poly DNB and 1-phr Antioxidant 2246.....	120
5.6.....Shift Constants and Polynomial Coefficients for Resin-Cured Chlorobutyl Formulations.....	121
5.7.....Formulations and Representative Physical Properties of Resin-Cured Chlorobutyl at Varying Loadings of N347 Black.....	123
5.8.....Formulations and Representative Physical Properties of Resin-Cured Chlorobutyl at Varying Loadings of Mica.....	124
5.9.....Shift Constants and Polynomial Coefficients for Mica-Filled Chlorobutyl Formulations.....	125

Chapter 6:

6.1.....EPDM Nordel Compounds.....	129
6.2.....EPDM Royalene 521 Compounds.....	130
6.3.....Polynomial Coefficients and Shift Constants for EPDM Formulations.....	132
6.4.....EPDM Formulation 259-1.....	133

6.5.....EPDM Formulation Royalene 400.....	136
--	-----

Chapter 7:

7.1.....Viton A Formulation.....	142
7.2.....Viton B Formulations.....	143

Chapter 8:

8.1.....MINSY Natural Rubber.....	147
8.2.....DTNSRDC 334-291 Natural Rubber.....	148

Chapter 9:

9.1.....Formulations and Physical Properties of Neoprene GRT with 30-phr Loading of Different Carbon Blacks.....	158
9.2.....Polynomial Coefficients and Shift Constants for Neoprene GRT Compounds with 30-phr Loading of Different Blacks.....	159
9.3.....Formulations and Physical Properties of Neoprene WRT Compounds with Varying Loadings of N660 Black.....	163
9.4.....Formulations for Additional Neoprene Compounds.....	164

Chapter 10:

10.1....NSWC Paracril CLT Formulations.....	170
10.2....NSWC Paracril CLT Formulations with Iron Oxide Filler.....	172
10.3....NSWC Paracril CLT Formulations with Silica Filler.....	175
10.4....NSWC Nitrile Formulations with Saret 500 Peroxide Cure.....	177
10.5....NSWC Paracril CLT Formulations with Saret 515 Peroxide Cure.....	179
10.6....NSWC Paracril CLT Formulations with Peroxide Cure and Different Fillers.....	181

10.7....NBR Formulations with Varying ACN Content.....	184
10.8....Nitrile Formulations with 26% ACN Content and Varying Loadings of Carbon Black.....	186

Chapter 12:

12.1....Polybutadiene Formulation.....	219
12.2....Hypalon Formulation CE-165-3.....	220
12.3....SBR Formulation AA-165-8.....	221

Appendix 5:

A5.1....Compressibility of Baker dB-grade Castor Oil.....	250
A5.2....Thermal Expansion of Baker dB-grade Castor Oil.....	251

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KEY WORD LOCATOR

Abrasion resistance

- definition of.....289
- in elastomers.....75, 156, 168, 191, 215,
222
- test for.....289

Accelerators

- general discussion of.....50, 61
- use in compounds of
 - butyl.....107, 108, 110
 - chlorobutyl.....108, 110, 111, 123, 124
 - EPDM.....130, 133
 - natural rubber.....147, 148
 - neoprene.....156, 158, 163, 164
 - nitrile.....168, 170, 172, 175, 177,
179, 181, 184, 186
 - SBR.....221
 - sulfenamide.....61
 - thiazole (ALTAX).....61, 107, 128
 - thiuram (SULFADS, TUADS, UNADS).....61, 107, 128
- Acoustic coupling fluids.....191, 243
- Acoustic impedance.....33, 34, 89, 244, 246,
248, 260, 289
- Acrylonitrile, comonomer nitrile rubber (NBR).....74
 - effect of acrylonitrile content
on properties.....167, 169, 183-185
 - effect of carbon black loading.....167, 170, 171, 186, 187

Adhesion

ASTM adhesion tests.....	86
characterization of failures.....	86, 87
general discussion of.....	80-87
testing, rubber-to-metal bonding.....	86, 87

Antioxidants

discussion of.....	70-72
use in base compounds of	
butyl.....	107, 108, 110
chlorobutyl.....	108, 110, 111, 123, 124
EPDM.....	130, 133
natural rubber.....	147, 148
neoprene.....	156, 158, 163, 164
nitrile.....	168, 170, 172, 175, 177, 179, 181, 184, 186

Antiozonants, description.....73

Attenuated total reflection spectroscopy.....46, 47

Attenuation.....26, 36-39, 89, 95, 243, 258-260

Bulk compliance.....6, 20, 32, 33

Bulk compression.....7

Bulk longitudinal deformation.....7

Bulk modulus

adiabatic.....	6, 33
isothermal.....	6
longitudinal.....	7, 160, 161
loss.....	5
storage.....	5

Butyl rubber (IIR).....	71, 73, 105, 106, 108-110
Carbon black - see "Fillers"	
Castor oil	
dB Grade.....	246-254, 256
Lubricin.....	254
Chlorobutyl rubber (CIIR).....	13, 14, 55, 92-94, 107-115, 249, 254-256
cure systems for.....	107-115
effects of fillers on viscoelastic properties.....	116-125
Chlorosulfonated polyethylene rubber (CSM).....	46, 74, 168, 222, 230 (also see "Hypalon")
Compliance	
loss, in bulk deformation.....	6
loss, in extension.....	7
loss, in shear.....	6
storage, in bulk deformation.....	6
storage, in extension.....	7
storage, in shear.....	6
Compounding of elastomers.....	57-74
Copolymers.....	24, 54, 59, 137, 167, 189
Compressibility.....	20
of castor oil.....	250
of polyalkylene glycol.....	256
Compression molding.....	78, 79
Compression set.....	89, 128, 138, 145, 167, 203-205, 207, 289
Creep.....	26, 27, 62, 75, 89, 168

Crosslinking

effects of.....81, 62

systems.....61, 62

Cure accelerators.....77, 108, 155

Cure activators.....55, 146

Damping

constrained-layer.....97, 98, 101-103

free-layer.....95-98, 100

internal, in rubbers.....5, 28, 106

Dielectric constant.....290

Dielectric permittivity.....51

Dielectric spectroscopy.....51, 52

Differential

scanning calorimetry.....19, 52-54

thermal analysis.....52, 54

Dinitrosobenzene.....107, 117, 146

Dithiocarbamate.....60, 61, 73, 107, 128

Dynamic mechanical analysis.....24, 52, 54

Dynamic mechanical analyzer.....27, 31

Dynamic mechanical spectroscopy.....27, 76, 77

Dynamic mechanical thermal analyzer.....27

Elastomers

aging properties of.....74

compounding of - see "Compounding"

crosslinking in - see "Crosslinking"

definition of.....1

fillers in.....62-69

- gum stocks.....58, 59, 225-231
- vulcanization of.....74-77
- Electric dissipation factor.....290
- Ethylene-propylene-diene monomer rubber (EPDM)....24, 70, 74, 81, 127-136,
225, 230, 231
- Ethylene thiourea.....112, 114, 120, 155, 156
- Fillers
- effect on rubber properties.....62-69
- Fitzgerald transducer.....28, 29, 189
- Flex cracking.....72, 146
- Fluorocarbon elastomers (CFM).....137-144, 225, 230, 231,
255
- Forced vibration measurement systems.....25-29
- Fourier transform infrared spectroscopy.....41-51
- Free volume.....8, 20, 70
- Frequency dependence of dynamic
mechanical properties.....11-21
- Frequency temperature relations for
dynamic mechanical properties11-21
- Frequency transmissibility curves
- dependence of carbon black content
 in chlorobutyl rubbers.....92-95
- Glass transition
- definition of.....18
- dependence on pressure.....20, 21
- dependence on time scale of experiment.....15, 19
- Hardness
- definition of.....200
- effect of carbon black fillers on.....64, 65
- effect of crosslinking on.....62

relationship between Shore A hardness and static Young's modulus.....	263
Heat build up in elastomers.....	72, 167
Hypalon (OSM).....	217, 220, 222, 230
Impedance tube.....	33-37
Injection molding.....	78, 79
Internal reflection spectroscopy.....	39, 46-48
Isobutylene-isoprene rubbers (IIR).....	105-110, 225, 229, 231
Isolators, vibration.....	60-65
Inopar.....	254, 255
Lead oxide.....	107, 146
Logarithmic decrement.....	28
Longitudinal storage modulus - see "Modulus"	
Loss modulus	
in bulk deformation.....	6, 7
in extension.....	7
in shear.....	5
Loss tangent definition.....	5
Loss tangent temperature-frequency relationship...	12-14
Low temperature stiffness.....	290
MPTS (2, 2' di-benzothiazyl disulfide)	
use as cure accelerator.....	107, 111, 123, 124, 146
Metravib.....	27
Mica.....	121, 122, 124, 125
Michelson interferometer.....	42

Modulus

bulk.....	6
bulk longitudinal.....	7, 160, 161
loss.....	5-7
shear.....	5
storage.....	5
temperature-frequency relationship.....	12-14
Young's.....	7
Mooney viscometer.....	75, 76
Konsanto oscillating disk rheometer.....	75, 76
NA-22 - see "ethylene thiourea"	
Natural rubbers (NR).....	141
classifications.....	141
cure systems.....	146-148
fillers.....	147-149
Neoprene rubbers (CR).....	155
GRT.....	155
WRT.....	155
cure systems.....	155, 156
fillers.....	156
specific formulations.....	157-165
Nitrile rubbers (NBR).....	167
cure systems.....	167, 168
fillers.....	168
specific formulations.....	169-187
Nuclear magnetic resonance (NMR).....	23

Octamine, use as antioxidant in

natural rubber.....	147, 148
neoprene.....	156, 158, 163, 164
nitrile.....	108, 170, 172, 175, 177, 179, 181, 184, 186

Oil resistance.....	106, 137, 146, 156, 168, 222, 223
---------------------	--------------------------------------

Ozone

cracking.....	73
protection.....	49
resistance.....	73, 74, 127, 146, 156, 168, 214, 222, 223, 290

Photoacoustic spectroscopy.....	50, 51
---------------------------------	--------

Plasticizers.....	69, 70, 157, 244, 245
-------------------	-----------------------

Poisson's ratio.....	8, 99
----------------------	-------

Polyalkylene glycol.....	255, 256
--------------------------	----------

Polyalphaolefin.....	257
----------------------	-----

Polybutadiene rubber.....	215, 216, 219
---------------------------	---------------

Polyurethanes (U)

general discussion of.....	189-192
commercial formulations.....	192-241

Red lead

use in chlorobutyl cure systems.....	92, 97, 112, 117, 120
use in neoprene cure systems.....	155, 158, 159, 163, 164

Resonance

measurement systems for dynamic mechanical properties.....	29-32
of simple mount.....	91, 92, 95

Rheovibron.....	26
-----------------	----

Rheometrics dynamic mechanical spectrometer.....	27, 76
Schenectady SP1055 resin.....	108, 111, 117, 123, 124
Shear modulus	
definition of.....	4, 5
of Viton A.....	139
Shell Sol.....	257, 258
Shrinkage, in rubber articles.....	80
Silicone fluid.....	258-260
Simple mount system.....	91
Sorbothane.....	200, 201, 214
Sound velocity	
calculation from values of moduli.....	10, 11
in castor oil as function of temperature.....	243
in coupling fluids as function of temperature.....	247
in Isopar.....	254
in polyalkylene glycol.....	256
in polyalphaolefin.....	257
in selected metals.....	261
in silicone fluids.....	258-260
Strain, sinusoidal.....	3
Stress, sinusoidal.....	3, 4, 26
Structural damping - see "damping"	
Styrene-butadiene rubber (SBR).....	24, 70, 215, 218, 221, 227, 229, 230, 231
Sulfur.....	60, 77, 107, 128, 148, 167
Swelling.....	105, 156, 168, 244, 255, 258

Tear strength.....	62, 64, 289
in chlorobutyl rubbers.....	120, 123, 124
in EPDM rubbers.....	129, 130, 133
in polyurethanes.....	204-210, 213, 214
Tensile strength.....	62, 64, 289
in butyl and chlorobutyl rubber.....	105, 110, 112, 117, 120, 123, 124
in EPDM rubber.....	128-130, 133
in fluorocarbon rubber.....	142
in Hypalon rubber.....	220
in natural rubber.....	147
in neoprene rubber.....	158, 163
in nitrile rubber.....	167
in polyurethanes.....	202-214
in styrene-butadiene rubber.....	221
Thermal expansion	
coefficient of.....	80
in polyurethane PR 1538.....	204
in acoustic coupling fluids.....	243, 251, 257-259
Thermogravimetric analysis.....	53, 55, 56
Torsional pendulum.....	20, 28
Transfer molding.....	77, 79, 80
Transmission spectroscopy (IR).....	44-46
Ultrasonic techniques.....	24, 37-39
Urethanes - see "Polyurethanes"	
Ultraviolet (UV) radiation.....	72, 73, 138
absorbers.....	72, 73
protection against.....	72, 73

tests for aging.....	73
Vibration isolation.....	30-95
Viscoelastic	
linear behavior.....	25, 26, 29, 69, 130
materials.....	3-11, 36, 99
Viton (CFM).....	137-144, 231
Vulcanization, general discussion of.....	74-80
Williams-Landel-Ferry (WLF) equation.....	17
Young's modulus	
definition of.....	7
relationship of static to Shore A hardness.....	263
Zinc oxide.....	60-62, 107, 109, 110-112, 114, 115, 117, 123, 124, 128-130, 133, 136, 155, 168